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## CONTENTS

### SECTION A.—PHYSICAL SCIENCES

Page

The Theory of Some A-C. Commutator Motors with Series Characteristics. I. The Repulsion Motor—*E. G. Cullwick* 49

### SECTION B.—CHEMICAL SCIENCES

Note on the Pyrolysis of Methyl and Ethyl Cyanides—*B. S. Rabinovitch and C. A. Winkler* - - - - - - - - - 69

The Hydrolysis of Acid Amides in Concentrated Hydrochloric Acid Solutions—*B. S. Rabinovitch and C. A. Winkler* - - 73

Pasture Studies. XXIII. A Proposed Modification of the Fluorimetric Method for the Estimation of Riboflavin —*R. A. Chapman and W. D. McFarlane* - - - - - 82

The Alkaloids of *Lycopodium* Species. I. *Lycopodium complanatum* L.—*R. H. F. Manske and Léo Marion* - - - 87

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VOL. 20, SEC. A. MAY, 1942 NUMBER 5

# THE THEORY OF SOME A-C. COMMUTATOR MOTORS WITH SERIES CHARACTERISTICS

## I. THE REPULSION MOTOR[1]

BY E. G. CULLWICK[2]

## Abstract

A general method, using "full reactances", is applied for developing the theory of the simple repulsion motor, the compensated repulsion motor, and the three-phase series motor. The effect of the currents induced in the armature turns short-circuited by the brushes is included, and is shown to affect profoundly the operation of the motors. Graphical constructions for the current loci are given, together with methods of measuring the various reactances, and of accounting for the effect of saturation. Experimental results for a three-phase series motor are included and compared with calculated values.

Part I, published below, deals with the simple repulsion motor. Neglecting the effects of the coils short-circuited by the brushes, the usual well known results are obtained, and the position of the brushes for maximum starting torque is studied. The currents circulating in the coils short-circuited by the brushes are then found to have the following effects:

(*a*) The performance of the motor, for a given current, is improved at speeds below synchronism, and is impaired at speeds above synchronism.

(*b*) The maximum power factor is found to occur at some finite speed, whereas, if the effect of the short-circuited coils is neglected the power factor is a maximum at infinite speed.

(*c*) The no-load speed is considerably lower than that usually associated with series motors.

The rise and fall of the currents in the coils short-circuited by the brushes is studied in the Appendix.

## List of Symbols

$a, b$ = effective turns ratio, stator to rotor;
$a, a_t$ = transformation ratio of transformer;
$A$ = resultant magnetomotive force;
$A_1, A_2$ = magnetomotive forces, exerted by stator and rotor;
$c$ = a constant;
$e$ = base of natural logarithms;
$e, E$ = e.m.f., instantaneous and r.m.s. values, in volts;
$e_r, E_r$ = rotational e.m.f.;
$e_t, E_t$ = transformer e.m.f.;
$f$ = frequency of supply, cycles per second;

[1] *Manuscript received in original form October 28, 1941, and as revised February 9, 1942. Contribution from the Department of Electrical Engineering, University of Alberta, Edmonton, Alta.*

[2] *Professor and Head of the Department.*

$i$, $I$ = current, instantaneous and r.m.s. values, in amperes;
$I_1$, $I_2$ = stator and rotor currents;
$I'$ = $yI$, effective magnetizing current;
$j$ = vector operator;
$k_1$, $k_2$ = winding coefficients, stator and rotor;
$L$ = coefficient of self-induction;
$M$ = coefficient of mutual induction;
$N_1$, $N_2$ = number of turns per phase, stator and rotor windings;
$n$ = rotational speed, revolutions per second;
$n_s$ = synchronous speed;
$n_0$ = minimum stable speed;
$p$ = number of poles;
$P_c$ = copper loss;
$P_m$ = gross motor power, per phase, in watts;
$q$ = pulsation;
$Q$ = $\sqrt{2}\,N\,p$;
$r$, $R$ = resistance, ohms;
$R_1$ = resistance of stator winding, per phase;
$R_2$ = resistance of rotor circuit, per phase;
$T$ = torque, per phase, lb.-ft.;
$T_S$ = starting torque, per phase;
$t$ = time, in seconds;
$V$ = potential difference, r.m.s. value, volts;
$W$ = power, watts;
$X$ = reactance, ohms;
$X_1$ = total reactance of stator, per phase;
$X_2$ = total reactance of rotor, per phase;
$X_{12}$ = maximum mutual reactance, between stator and rotor;
$x_1$, $x_2$ = stator and rotor leakage reactance;
$x_e$ = total equivalent leakage reactance, referred to stator;
$Z$ = impedance, ohms;
$R_e$, $X_e$, $Z_e$ = equivalent standstill resistance, reactance and impedance of motor, per phase;
$R'_e$, $X'_e$, $Z'_e$ = equivalent standstill values, taking into account the effect of the short-circuited coils;
$R_{et}$, $X_{et}$, $Z_{et}$ = total equivalent values of motor, neglecting the effect of the short-circuited coils;
$R'_{et}$, $X'_{et}$, $Z'_{et}$ = total equivalent values, taking into account the effect of the the short-circuited coils;
$R_s$, $X_s$, $Z_s$ = resistance, etc., of the short-circuited coil;
$R_c$, $X_c$ = maximum values of the resistance and reactance of the short-circuited coils, referred to the stator;
$X_{sm}$ = maximum mutual reactance, between stator and short-circuited coils;
$X_{rm}$ = maximum mutual reactance, between rotor and short-circuited coils;
$\alpha$, $\beta$, $\gamma$, $\eta$, $\theta$, $\psi$ = angles;

$y = A/A_1$ ;
$\phi$ = resultant mutual flux, in webers;
$\phi_1$ , $\phi_2$ = mutual fluxes of $I_1$ and $I_2$ ;
$\phi_{L_1}$ , $\phi_{L_2}$ = leakage fluxes of $I_1$ and $I_2$ ;
$\phi_s$ = speed component of flux;
$\phi_t$ = transformer component of flux;
$\omega$ = pulsation of supply, $2\pi f$.

***Boldface Italic type*** is used for quantities that are time-vectors expressed in complex notation, such as: $\boldsymbol{Z} = R + jX$. The scalar magnitude of the quantity, $\sqrt{R^2 + X^2}$, is denoted by $Z$.

## Introduction

Much has been written on the mathematical theory of a-c. commutator motors with series characteristics, particularly in German literature, but no comparatively simple "working theory" seems to exist whereby the performance of such motors can be predetermined with a fair degree of accuracy. One of the best treatments, in the English language, of single-phase series motors is that of Steinmetz (3, pp. 499-556), who was one of the first to apply the modern methods of complex algebra to such cases. Steinmetz studied the effects of the circulating current in the coils short-circuited by the brushes, and found them to be considerable. Indeed, unless these effects and those of saturation of the iron are taken into account, a reasonable degree of accuracy in the forecasting of performance cannot be obtained.

The method to be developed in this paper has its origin in the work of Steinmetz and also in certain lectures given by Dr. C. G. Lamb, some years ago, in the Engineering School at Cambridge University.

## The Repulsion Motor

### 1. *Fundamental Relations*

Consider a single-phase stator winding, carrying an alternating current of sinusoidal wave-form and frequency $f = \omega/2\pi$. The space-distribution of the air-gap flux-density of the magnetic field will depend on the configuration of the winding, and in all cases it may be analysed into sinusoidal harmonic components.

Suppose a single-phase rotor with a commutator rotates in the alternating magnetic field of the stator. If alternating current of the same frequency as that of the stator current is led through this rotor winding by means of brushes $b$ and $b'$, the stator and rotor currents will combine to set up a resultant alternating flux of amplitude $\phi$. Let the angle between the flux-axis and the brush-axis be $\alpha$ (Figs. 1*a* and 1*b*). Confining the analysis to the fundamental component of the space-distribution of resultant air-gap flux-density, we may resolve the total flux $\phi$ into two components:

(1) the *speed* flux, $\phi_s = \phi \sin \alpha$, perpendicular to the brush-axis;

(2) the *transformer* flux, $\phi_t = \phi \cos \alpha$, along the brush-axis.

Adopt the convention that the sense of the rotor winding between the brushes is right-handed. Then the r.m.s. value of the e.m.f. induced between the brushes, from $b$ to $b'$, is

$$E_{bb'} = Q(n\phi_s + jn_s\phi_t) \tag{1}$$

in the case of Fig. 1*a*, in which the positive direction of $\phi_s$ is $\pi/2$ in *advance* of the positive direction of $\phi_t$, and

$$E_{bb'} = Q(-n\phi_s + jn_s\phi_t) \tag{2}$$

in the case of Fig. 1*b*, in which the positive direction of $\phi_s$ *lags* by $\pi/2$ behind the positive direction of $\phi_t$.

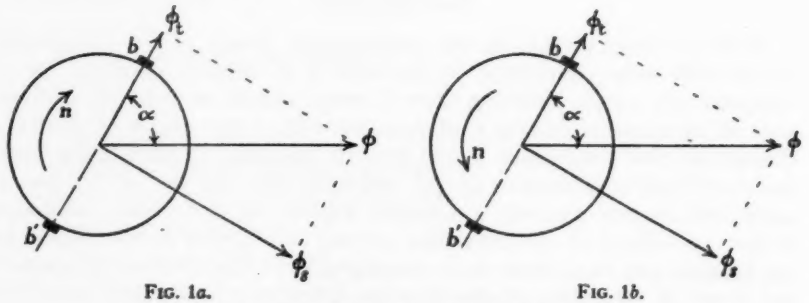


FIG. 1a. FIG. 1b.

FIG. 1. *Speed and transformer fluxes.*

In these equations, $Q = \sqrt{2}\,Np$, where $N$ is the number of turns in series in the rotor winding, $p$ is the number of poles, $n$ the rotational speed and $n_s$ the synchronous speed; the first term of each expression, (1) and (2), is the *rotational* e.m.f., whereas the second gives the *transformer* e.m.f.*

The quantity $Q$ is related to the reactances of the windings as follows. Suppose a current $I$ flowing in both stator and rotor sets up a resultant mutual flux $\phi$, made up of components $\phi_1$ due to the stator and $\phi_2$ due to the rotor windings; there will also be leakage fluxes $\phi_{L_1}$ and $\phi_{L_2}$. Then, if $Q_1 = \sqrt{2}\,N_1p$ and $Q_2 = \sqrt{2}N_2p$:

$$Q_1n_s(\phi_1 + \phi_{L_1}) = IX_1, \tag{3}$$

$$Q_2n_s(\phi_2 + \phi_{L_2}) = IX_2, \tag{4}$$

and

$$Q_2n_s\phi_1 = Q_1n_s\phi_2 = IX_{12}, \tag{5}$$

where $X_1$ and $X_2$ are the total reactances of stator and rotor respectively, and $X_{12}$ is the mutual reactance between the two windings.

* *The rotor winding is assumed to be full-pitch and uniformly distributed. For example, consider the rotational e.m.f.: this is due only to the rotational e.m.f's in bands of conductors of width* $2\alpha$ *(Fig. 1a). The breadth coefficient of these bands is* $\sin\alpha/\alpha$, *and the number of turns in them is* $2\alpha N/\pi$. *Hence the rotational e.m.f. is easily seen to be* $2N\phi pn \sin\alpha \sin\omega t$, *which has an r.m.s. value* $E_r = \sqrt{2}\,Np\phi n \sin\alpha = Qn\phi_s$. *The transformer e.m.f. is obtained in a similar manner.*

*Relation Between the Total and Leakage Reactances*

If $a$ is the effective turns ratio between stator and rotor, $x_1$ and $x_2$ are the leakage reactances of stator and rotor respectively, and $x_s = x_1 + a^2x_2$, the total equivalent leakage reactance of the machine referred to the stator, then it can be shown that

$$X_{12} = \sqrt{X_1X_2} - \frac{x_s}{2a} \tag{6}$$

to a very high degree of accuracy. Another form of this equation is

$$X_1X_2 \doteq X_{12}\left(X_{12} + \frac{x_s}{a}\right), \tag{6a}$$

since $x_s$ is small compared with $X_1$, $X_2$, and $X_{12}$.

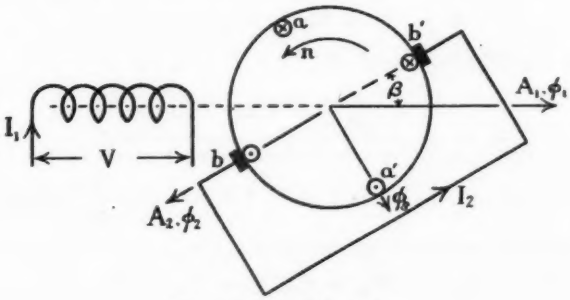


FIG. 2. *Repulsion motor.*

## 2. *General Theory of the Repulsion Motor*

In the simple repulsion motor shown diagrammatically in Fig. 2* the direction of rotation will be counter-clockwise; for if at the instant considered the stator magnetomotive force (m.m.f.) $A_1$ is from left to right, the m.m.f. $A_2$ of the induced armature currents must be from $b'$ to $b$ (i.e., it must have a component opposed to $A_1$) and the direction of the armature currents is downwards at $a$ and upwards at $a'$. The arbitrarily chosen positive directions of the various quantities are shown by the arrows. We shall first neglect the effect of the coils short-circuited by the brushes.

The mutual flux $\phi$ may be resolved into stator and rotor components $\phi_1$ and $\phi_2$, assumed to have sinusoidal distribution in space. In addition there are the stator leakage flux $\phi_{L_1}$ along the stator axis and the rotor leakage flux $\phi_{L_2}$ along the brush axis. Resolving perpendicularly to $bb'$, we find for the speed flux

$$\phi_s = \phi_1 \sin \beta. \tag{7}$$

The rotational e.m.f. from $b'$ to $b$ is, from Equation (1),

$$E_r = -Q_2 n \phi_s = -X_{12}\frac{n}{n_s} I_1 \sin \beta. \tag{8}$$

It should be noted that the stator leakage flux $\phi_{L1}$ induces no e.m.f. in the rotor, and that the rotor leakage flux is along the brush axis and hence induces no rotational e.m.f. between the brushes. Equation (8) arises from the fact

* *See also Fig. 8.*

that $Q_2 n_s \phi_1$ is the transformer e.m.f. induced in the rotor, when $\beta = 0$, by the stator component of the mutual flux; i.e., it is equal to $I_1 X_{12}$, where $X_{12}$ is the maximum mutual reactance between stator and rotor. The transformer e.m.f. from $b'$ to $b$, due to the mutual flux, is

$$E_{mt} = -jQ_2 n_s(\phi_2 - \phi_1 \cos \beta).$$

The rotor leakage flux $\phi_{L_2}$ causes an additional e.m.f. $-jQ_2 n_s \phi_{L_2}$, so that the total transformer e.m.f. is

$$E_t = -j(I_2 X_2 - I_1 X_{12} \cos \beta). \tag{9}$$

Thus, for the rotor circuit, if $E$ is the total resultant e.m.f. due to all causes,

$$E = E_r + E_t = I_2 R_2,$$

so that, from Equations (8) and (9)

$$I_2 = -\frac{I_1\left[\frac{n}{n_s} X_{12} \sin \beta - jX_{12} \cos \beta\right]}{R_2 + jX_2} \tag{10}$$

$$= \frac{I_1}{Z_2^2}\left\{\left(X_2 X_{12} \cos \beta - \frac{n}{n_s} R_2 X_{12} \sin \beta\right) + j\left(R_2 X_{12} \cos \beta + \frac{n}{n_s} X_2 X_{12} \sin \beta\right)\right\}. \tag{11}$$

The stator terminal potential difference (p.d.) is

$$V = I_1(R_1 + jX_1) - jI_2 X_{12} \cos \beta = I_1 Z_{st}, \tag{12}$$

where

$$Z_{st} = \left[R_1 + R_2\left(\frac{X_{12}}{Z_2}\right)^2 \cos^2 \beta\right] + j\left[X_1 - X_2\left(\frac{X_{12}}{Z_2}\right)^2 \cos^2 \beta\right] + \frac{n}{n_s}\left(\frac{X_{12}}{Z_2}\right)^2 \frac{\sin 2\beta}{2}(X_2 + jR_2), \tag{13}$$

and may be called the "total equivalent impedance". Equation (12) may be written:

$$V = I_1(R_s + jX_s) - E_r,$$

where

$$\left.\begin{aligned} R_s &= R_1 + R_2\left(\frac{X_{12}}{Z_2}\right)^2 \cos^2 \beta, \text{ the equivalent standstill resistance,} \\ X_s &= X_1 - X_2\left(\frac{X_{12}}{Z_2}\right)^2 \cos^2 \beta, \text{ the equivalent standstill reactance,} \\ \text{and} \\ E_r &= -\frac{n}{n_s}\left(\frac{X_{12}}{Z_2}\right)^2 \frac{\sin 2\beta}{2}(X_2 + jR_2) I_1, \text{ the rotational e.m.f., referred to the stator.} \end{aligned}\right\} \tag{15}$$

The vector diagram is shown in Fig. 3.

*The copper loss* is $P_c = I_1^2 R_1 + I_2^2 R_2$. Whence, from Equation (10), the equivalent resistance of the motor when running is

$$\frac{P_c}{I_1^2} = R_1 + R_2\left(\frac{X_{12}}{Z_2}\right)^2 \left(\cos^2 \beta + \frac{n^2}{n_s^2} \sin^2 \beta\right). \tag{16}$$

*The gross motor power* is equal to the input less the copper loss, or:

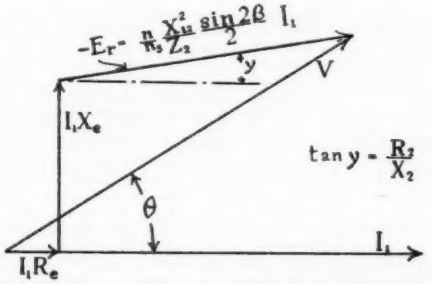


FIG. 3. *Repulsion motor. Vector diagram, neglecting short-circuit currents.*

$$P_m = I_1^2 \frac{n}{n_s}\left(\frac{X_{12}}{Z_2}\right)^2 \sin\beta\left\{X_2\cos\beta - \frac{n}{n_s}R_2\sin\beta\right\}. \tag{17}$$

*The gross torque* is

$$T = 0.117\frac{P_m}{n}. \tag{17a}$$

*The starting torque:* from Equations (12) and (17*a*), putting $n = 0$,

$$T_S = 0.117\, V^2 \frac{X_2}{2n_s}\left(\frac{X_{12}}{Z_2}\right)^2 \times \frac{\sin 2\beta}{\left[R_1 + R_2\left(\frac{X_{12}}{Z_2}\right)^2\cos^2\beta\right]^2 + \left[X_1 - X_2\left(\frac{X_{12}}{Z_2}\right)^2\cos^2\beta\right]^2}. \tag{18}$$

This is a maximum, for a given *current*, when $\beta = 45°$. For a given *terminal p.d.*, if resistance is neglected the following condition for maximum starting torque is obtained by differentiation:

$$\cos^2 2\beta + \left(\frac{2X_1X_2}{X_{12}^2} - 1\right)\cos 2\beta - 2 = 0 \tag{19}*$$

If there is no leakage, this gives $\beta = 0$. Fig. 4 gives the solution of Equation (19) for different values of $X_1X_2/X_{12}^2$, or $1 + x_s/aX_{12}$ (See Equation (6*a*) ).

### 3. *Rough Approximations*

If resistance and leakage are neglected ("ideal" motor), we may put $R_1 = R_2 = 0$, $X_1 = cN_1^2$, $X_2 = cN_2^2$, $X_{12} = cN_1N_2$, where $c$ is a constant. Whence

$$Z_a \doteq X_1\sin\beta\sqrt{\left(\frac{n}{n_s}\right)^2\cos^2\beta + \sin^2\beta}. \tag{20}$$

The *power factor* is then

$$\cos\theta \doteq \frac{\frac{n}{n_s}\cos\beta}{\sqrt{\left(\frac{n}{n_s}\right)^2\cos^2\beta + \sin^2\beta}}, \tag{21}$$

* *F. W. Carter (1, p. 949) gives this result in the form:* $\tan^2\beta = \sqrt{1 - xx' + \frac{9}{4}(xx')^2} - \frac{3}{2}xx'$, *where* $x = \frac{X_{12}}{aX_1}$, $x' = \frac{aX_{12}}{X_2}$.

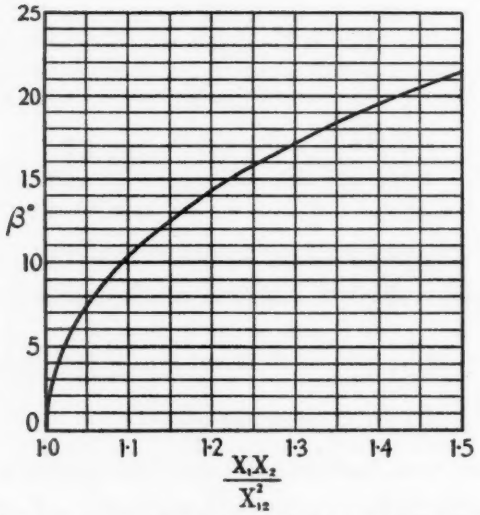


FIG. 4. *Repulsion motor. Brush-shift angle β for maximum starting torque.*

whence

$$\left(\frac{n_s}{n}\right)^2 \tan^2 \beta \doteq \frac{1}{(p \cdot f)^2} - 1. \tag{22}$$

That is, the power factor will remain approximately constant if tan $\beta$ is made proportional to the speed. At synchronous speed, from Equation (21):

$$\cos \theta \doteq \cos \beta \tag{23}$$

4. *Relation Between the Transformer and Speed Fluxes, $\phi_t$ and $\phi_s$.*

If the winding coefficients of the stator and rotor windings are the same,

$$\phi_s = \phi_1 \sin \beta = KI_1N_1 \sin \beta, \tag{24}$$

where $K$ is a constant, and

$$\phi_t = K(I_2N_2 - I_1N_1 \cos \beta). \tag{25}$$

Substituting for $I_2$ from Equation (11), and neglecting resistance and leakage we find that

$$\phi_t \doteq jKI_1 \frac{n}{n_s} N_1 \sin \beta \doteq j \frac{n}{n_s} \phi_s. \tag{26}$$

Hence $\phi_t$ and $\phi_s$ are approximately in time quadrature. Since they are also in space quadrature it follows that they combine to form a "rotating field" whose speed is $n_s$ in the same direction as $n$. At synchronous speed this rotating field is approximately constant, but at other speeds its magnitude pulsates.

5. *Commutation in the Repulsion Motor*

The commutation of a repulsion motor is inherently good at synchronous speed, a fact that may be explained either by the rotating field or, as follows,

by the cancellation by the speed e.m.f. of the transformer e.m.f. induced in a coil short-circuited by a brush.

The flux $\phi_s$ induces a *transformer* e.m.f. in the coil (at $bb'$, Fig. 2), while $\phi_t$ $(= \phi_2 - \phi_1 \cos \beta)$ induces a *speed* e.m.f. For the short-circuited coil, therefore, $\phi_s$ is the *transformer* flux and $\phi_t$ the *speed* flux. Since (Fig. 2) the positive direction of $\phi_t$ lags behind the positive direction of $\phi_s$, Equation (2) applies.

The number of short-circuited coils will depend on the number of brush sets, and in the following all these coils will be treated as equivalent to one short-circuited coil whose turns are closely coupled. This approximation is equivalent to neglecting the leakage fluxes of the individual short-circuited coils.

The e.m.f. induced in the short-circuited coil by the mutual flux is therefore

$$E_s = Q_s(-n\phi_t + jn_s\phi_s) \tag{27}$$

in a direction opposed to $\phi_s$, where $\phi_s$ is proportional to the number of turns in the coil. Now $Q_s n_s \phi_1 = I_1 X_{sm}$, where $X_{sm}$ is the maximum mutual reactance between the stator winding and the short-circuited coil, so that from Equations (24) and (26)

$$E_s \doteq jI_1 X_{sm} \sin \beta \left(1 - \frac{n^2}{n_s^2}\right), \tag{28}$$

which is zero at synchronous speed.

If $N_s$ turns are short-circuited by the brushes, then, very approximately,

$$X_{sm} \doteq \frac{\pi N_s}{2N_2} X_{12}, \tag{29}$$

if the winding is full-pitch and uniformly distributed.

It is clear from Equation (28) that the e.m.f. in a shorted coil of a repulsion motor is small only at speeds near synchronism. At standstill and at speeds greater than about $\sqrt{2}\, n_s$ the inherent commutation is no better than that of a simple series motor.

### 6. *Effect of the Currents in the Short-circuited Coils on the Performance of the Repulsion Motor*

The currents induced in the short-circuited coils by the transformer effect of $\phi_s$ oppose the m.m.f. of the stator winding. Hence for a given value of $\phi$ the value of $I_1$ is increased. In addition, the short-circuit currents react with the transformer field $\phi_t$ to produce a torque whose direction depends on the speed. Since $\phi_s$ lags by approximately 90° in time-phase behind $\phi_t$, the transformer e.m.f. in the shorted coils due to $\phi_s$ will be 180° out of phase with $\phi_t$. That is, when $\phi_t$ is a maximum and in the direction $b'b$, the induced current in the shorted coil will be near its maximum value and in the direction indicated by the dotted and crossed circles near $b$ and $b'$ in Fig. 2. The direction of the torque due to these currents and $\phi_t$ is clearly in the direction of rotation, and this condition will hold provided that the quantity in brackets in Equation (28) is positive: i.e., below synchronous speed. Above syn-

chronism, $E_s$ reverses in sign (Equation (28)) and the commutation torque will oppose the main torque.

This effect, which tends to improve the performance below synchronism and to impair it at speeds above synchronism, is negligible in the simple series motor, since in this case the short-circuit currents and $\phi_s$ are nearly in time quadrature and give very little torque.

The torque due to the short-circuit currents in the repulsion motor may be calculated as follows.

The short-circuit current is, from Equation (28),

$$I_s = \frac{E_s}{R_s + jX_s} = \frac{jI_1X_{sm} \sin \beta(1 - n^2/n_s^2)(R_s - jX_s)}{Z_s^2}, \tag{30}$$

where $R_s + jX_s$ is the total impedance of the short-circuited coil, $R_s$ being the mean value of the resistance during the commutating period. The approximation involved in assuming that this impedance is independent of the variation of the period of short-circuit with varying speed is discussed in the Appendix. In terms of $X_2$ we have, as a rough approximation,

$$X_s = \frac{\pi}{2}\left(\frac{N_s}{N_2}\right)^2 X_2. \tag{31}$$

This current induces an e.m.f. in the stator:

$$E_{s1} = jI_sX_{sm} \sin \beta = -I_1\left(\frac{X_{sm}}{Z_s}\right)^2 \sin^2 \beta(1 - n^2/n_s^2)(R_s - jX_s), \tag{32}$$

and a rotational e.m.f. $E_{r1}$ between the brushes $bb'$ (see Note, p. 70). Neglecting $E_{r1}$, the stator terminal p.d. is

$$V = I_1(R_s + jX_s) - E_r - E_{s1} = I_1Z'_{s1},$$

so that the total equivalent impedance of the motor is increased by

$$Z' = \sin^2\beta(1 - n^2/n_s^2)(R_s - jX_s), \tag{33}$$

where

$$X_s = X_s\left(\frac{X_{sm}}{Z_s}\right)^2 \quad \text{and} \quad R_s = R_s\left(\frac{X_{sm}}{Z_s}\right)^2. \tag{34}$$

The copper loss in the shorted coil is

$$I_s^2R_s = \frac{E_s^2}{Z_s^2}R_s = I_1^2R_s \sin^2 \beta(1 - n^2/n_s^2)^2 \tag{35}$$

from Equations (28) and (34). Since the input is increased by $I_1^2R_s \sin^2\beta (1 - n^2/n_s^2)$, it follows that the *gross power* is increased by

$$P_{sc} = I_1^2R_s \sin^2 \beta \frac{n^2}{n_s^2}\left(1 - \frac{n^2}{n_s^2}\right) \tag{36}$$

and the *gross torque* is increased by

$$T_s = 0.117\, I_1^2R_s \sin^2 \beta \frac{n}{n_s^2}\left(1 - \frac{n^2}{n_s^2}\right). \tag{37}$$

It should be noticed that $T_s$ is zero both at standstill and at synchronism.

We therefore have the following final results, taking into account the effect of the short-circuited coils:

*The equivalent standstill resistance*

$$R_s' = R_1 + R_2\left(\frac{X_{12}}{Z_2}\right)^2 \cos^2\beta + R_c \sin^2\beta. \tag{38}$$

*The equivalent standstill reactance*

$$X_s' = X_1 - X_2\left(\frac{X_{12}}{Z_2}\right)^2 \cos^2\beta - X_c \sin^2\beta. \tag{39}$$

*The rotational e.m.f.* Adding the part of $\boldsymbol{E}_{s1}$ (Equation (32)) which is a function of the speed, to $\boldsymbol{E}_r$ (Equation (15)):

$$\boldsymbol{E}_r' = -\boldsymbol{I}_1\left\{\frac{n}{n_s}\left(\frac{X_{12}}{Z_2}\right)^2 \frac{\sin 2\beta}{2}\,(X_2 + jR_2) - \frac{n^2}{n_s^2}\sin^2\beta(R_c - jX_c)\right\}. \tag{40}$$

*The copper loss, $P_c'$*

$$\frac{P_c'}{I_1^2} = \frac{P_c}{I_1^2} + R_c \sin^2\beta\left(1 - \frac{n^2}{n_s^2}\right)^2, \text{ where } P_c/I_1^2 \text{ is given by Equation (16).} \tag{41}$$

*The gross motor power*

$$P_m' = P_m + I_1^2 R_c \sin^2\beta\,\frac{n^2}{n_s^2}\left(1 - \frac{n^2}{n_s^2}\right). \tag{42}$$

*The gross torque*

$$T' = 0.117\,\frac{P_m'}{n}. \tag{42a}$$

Equating $T'$ to zero gives a cubic equation for the maximum no-load speed of the motor, neglecting the rotational losses. For example, applying this to the numerical case to be worked out below, the equation is

$$\left(\frac{n}{n_s}\right)^3 - 0.785\,\frac{n}{n_s} - 4.43 = 0$$

which gives $n/n_s = 1.8$, or $n = 3240$ r.p.m.

The actual no-load speed would be less than this, on account of rotational losses. The short-circuited coils thus prevent the repulsion motor from attaining the excessively high no-load speeds which are a characteristic of series motors in general.

*The total equivalent impedance*

$$Z_{st}' = R_s + R_c \sin^2\beta\left(1 - \frac{n^2}{n_s^2}\right) + X_2\left(\frac{X_{12}}{Z_2}\right)^2 \frac{\sin 2\beta}{2}\,\frac{n}{n_s}$$
$$+ j\left\{X_s - X_c \sin^2\beta\left(1 - \frac{n^2}{n_s^2}\right) + R_2\left(\frac{X_{12}}{Z_2}\right)^2 \frac{\sin 2\beta}{2}\,\frac{n}{n_s}\right\}, \tag{43}$$

where $R_s$ and $X_s$ are given by Equation (15). We may put:

$$Z_{st}' = R_{st}' + jX_{st}'. \tag{44}$$

For a given speed $n$, the performance may be calculated as follows: $I_1 = V/Z_{st}'$, p.f. $= \cos\theta = R_{st}'/Z_{st}'$, copper loss $= P_c'$, input $= I_1^2 R_{st}'$, output $= P_m'$ − rotational losses. The gross torque is obtained from Equation (42*a*), and the starting torque by calculating $I_1$ for $n = 0$ and using Equation (42*a*).

The vector diagram is shown in Fig. 5.

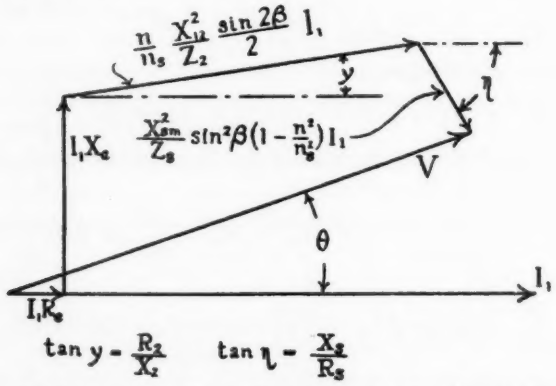


FIG. 5. *Repulsion motor. Vector diagram, allowing for short-circuit currents.*

### 7. *The Current Locus for Constant Reactances*

#### (a) *Neglecting the effect of the short-circuited coils*

To obtain the current locus by inversion we proceed as follows.

In Fig. 6 (see Equation (15)): $OX = X_e$, $XR = R_e$, $RN = -E_r/I_1$, $\tan y = R_2/X_2$. The primary current for the speed $n$ and terminal p.d. $V$ is then $I_1 = V/ON$, in phase and magnitude, and is represented by the vector $OP$ passing through $N$.

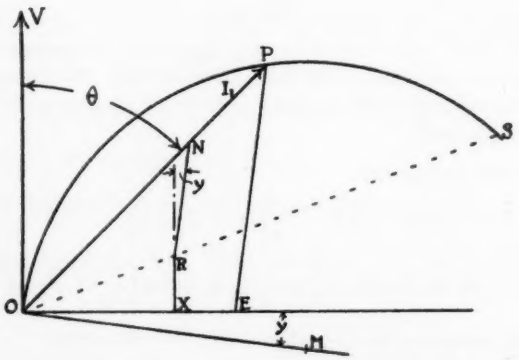


FIG. 6. *Repulsion motor. Circle diagram, neglecting short-circuit currents.*

The locus of $I_1$ is therefore the inverse of the line $RN$ with respect to the origin $O$. This is a circle of centre $M$ and passing through $O$. The standstill point is $S$, and the line $RN$ or any line parallel to it may be calibrated as a speed scale.

Allowance for core loss may be made in a well known manner, but for simplicity this is omitted. The various losses and the efficiency are given by intercepts on the line $PE$ parallel to $RN$.

It should be noticed that the maximum power factor occurs at infinite speed, and is equal to cos $y$. The effect of the short-circuited coils, however, is to make the maximum power factor occur at a finite speed, as will be seen below.

*(b) Allowing for the effect of the short-circuited coils*

Equation (43) may be rewritten as follows:

$$Z'_{s1} = \left\{ R_s + R_e \sin^2 \beta \right\} + j \left\{ X_s - X_e \sin^2 \beta \right\} - \frac{E_r}{I_1} - \frac{n^2}{n_s^2} \sin^2 \beta \, (R_e - jX_s), \tag{45}$$

where $R_s$, $X_s$, and $E_r$ are given by Equation (15) and refer to the case where the effect of the short-circuited coils is neglected.

Owing to the new term in $n^2$, the locus of the reflected impedance is no longer a straight line, but a parabola. This parabola may be constructed from the uncorrected case as follows.

In Fig. 7, $ON$ is the reflected impedance vector for the uncorrected case as in Fig. 6, and:

$$OX' = X'_s = OX - X_e \sin^2 \beta, \quad X'R' = R'_s = RX + R_e \sin^2 \beta.$$

$OR'$ is thus the reflected standstill impedance vector for the corrected case, and clearly

$$\tan \eta = X_s/R_s. \tag{46}$$

Now make $R'Q$ equal and parallel to $RN$. If it were not for the term in $n^2$ in Equation (45), $OQ$ would now give the reflected impedance for the corrected case. Locate $N'$ on the line $QN$ so that

$$QN' = \frac{n^2}{n_s^2} Z_e \sin^2 \beta. \tag{47}$$

Then $QN'$ represents the last term in Equation (45), and $ON'$ is the reflected impedance vector for the corrected case.

Since the correction disappears at synchronous speed, the loci of $N$ and $N'$ intersect at a point corresponding to synchronism. To locate $N'$ for any speed:

(1) Calibrate the line $RN$ as a uniform speed scale.

(2) Let the point $N$ represent a speed $n$. From $Q$ draw $QN' = \left(\frac{n}{n_s}\right)^2 R'R$.

For example, if $n$ is $\frac{1}{2}n_s$, then $QN' = \frac{1}{4}R'R$.

In this way the parabola $R'N' \ldots$ is easily constructed.

The current locus is the inverse of this parabola, and may be constructed point by point by measurement. It may, however, be obtained from the uncorrected circle locus of Fig. 6 by a simple geometrical construction.

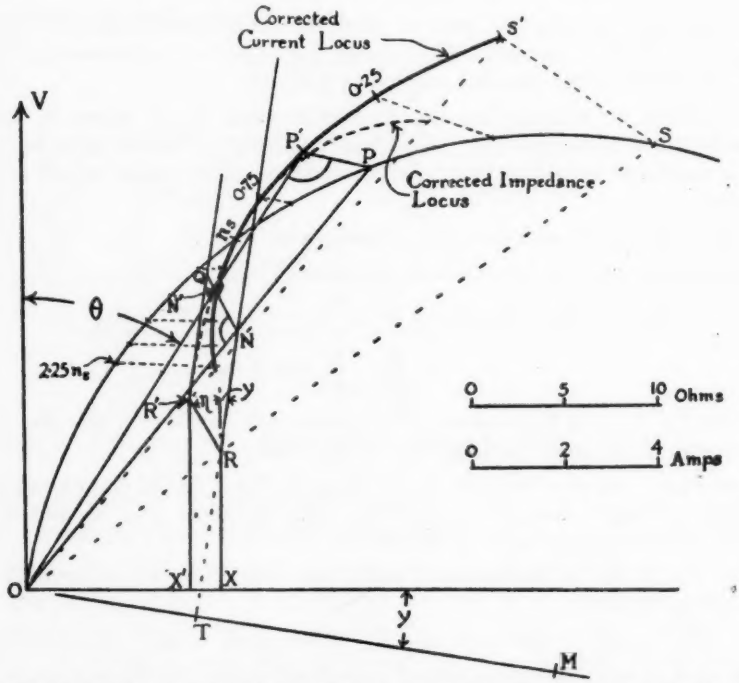


FIG. 7. *Repulsion motor. Construction of current locus, allowing for short-circuit currents.*

In Fig. 7, $N$ and $N'$ give the uncorrected and corrected impedances respectively for any speed $n$. $OP$ is the uncorrected current vector, $P$ lying on the circle which is the inverse of the line $RN$. On $ON'$ produced locate $P'$ such that $\angle PP'O = \angle N'NO$; then $OP'$ is the corrected current vector, for $OP'$. $ON' = OP \cdot ON$ = constant.

*Example.* Fig. 7 is drawn for the following case: $p = 4$; $f = 60$; $X_1 = 51.5$; $X_2 = 6.57$; $X_{12} = 17.4$; $R_1 = 1.38$; $R_2 = 0.98$; $Z_2 = 6.643$; $n_s = 1800$ r.p.m.; $V = 110$; $\beta = 18°$; h.p. $= \frac{1}{4}$; $N_2 = 144$; $N_s = 24$. From Equation (29) $X_m = \frac{1}{2}\pi 17.4/6 = 4.55$; from Equation (31) $X_s = \frac{1}{2}\pi 6.57/36 = 0.286$; Assuming $R_s = 0.5$ ohm, $Z_s = 0.576$, $X_s = 17.8$, $R_c = 31.2$. Then from Equation (15): $OX = 10.7$, $XR = 7.46$, $RN = \dfrac{n}{n_s}(13.24 + j\ 1.97)$. From Equation (45): $OX' = 9.0$, $X'R' = 10.44$, and

$$R'N' = \frac{n}{n_s}(13.24 + j\,1.97) - \left(\frac{n}{n_s}\right)^2 (2.98 - j\,1.7).$$

These values can be plotted to any convenient scale. The perpendicular $OT$ from $O$ to the line $RN$ is found to be 9.5 ohms, so that the diameter of the circle $OP$ is 110/9.5 = 11.6 amp. and its centre is on the line $OT$ produced.

The corrected locus is shown from standstill up to 2.25 $n_s$, but the no-load speed is less than 1.8 $n_s$, as we have seen above. The maximum power factor is found to be at about 1600 r.p.m.

Thus even with constant reactances (unsaturated iron) the current locus of a repulsion motor is not a circle.

8. *Measurement of the Reactances*

The total reactances $X_1$, $X_2$, and $X_{12}$ may be determined by simple voltmeter-ammeter tests.

The stator reactance $X_1$ should be measured for a range of primary current with the rotor brushes lifted, and $X_1$ should be plotted on a base of $I_1$.

The rotor reactance $X_2$ should be measured with the brushes down and the stator open-circuited. The coils short-circuited by the brushes have zero mutual reactance with the rotor winding, so do not affect the result. A curve of $X_2$ on a base of $I_2$ should be plotted.

To obtain the mutual reactance $X_{12}$ the brushes should be left down and the short-circuit lead between them opened. With the brushes set at $\beta = 0$, the brush p.d. should be measured for a range of *primary* current. Again, the short-circuited coils have zero mutual reactance with the stator. $X_{12}$ should be plotted on a base of $I_1$.

The equivalent leakage reactance, $x_s$, of the motor can be obtained by short-circuiting all the rotor coils by wrapping bare copper wire around the commutator, and by taking readings on the stator side.

The values of $X_1$ and $X_2$ are obtained approximately from the formula:

$$X = \frac{(V^2 - I^2R^2)^{\frac{1}{2}}}{I}, \tag{48}$$

where $V$ is the p.d. across the winding, $I$ the current, and $R$ the resistance. Owing to core loss, the flux lags behind the current by a small angle, and Equation (48) gives the reactance of the equivalent circuit and not the true reactance. If $W$ is the power taken, it is readily shown that the true reactance is given by

$$X = \frac{(V^2 + I^2R^2 - 2WR)^{\frac{1}{2}}}{I}, \tag{49}$$

but the two equations usually give results so nearly equal that the refinement obtained by using Equation (49) is not important.

The value of $X_{12}$ is given by

$$X_{12} = \frac{\text{p.d. between rotor brushes}}{\text{stator current}}. \tag{50}$$

9. *The Effect of Saturation*

The reactances as obtained above will be found to vary with the current. In general they will decrease as the current increases, and in an accurate predetermination of performance the effect of this variation must be taken into account.

The simplest method of doing this is to assume some arbitrary value of the stator current $I_1$. The values of the reactances for the state of saturation

caused by this current are substituted in Equation (43) which then gives a quadratic equation in $n/n_s$. The values of the reactances to be used, however, are not those that correspond directly to $I_1$ in the measurement of $X_1$, etc., since in these measurements only one winding carries current, and in actual operation the flux in the iron is a function of both stator and rotor currents, the speed, and the brush angle $\beta$.

If resistance and leakage reactance are neglected, and the stator and rotor winding factors are assumed equal, from Equation (24) :

$$\phi_s = \phi_1 \sin \beta = k A_1 \sin \beta$$

and

$$\phi_r = j \frac{n}{n_s} k A_1 \sin \beta = j k A_1 \sin \beta \left(1 + \frac{n}{n_s} - 1\right),$$

where the factor $k$ will depend on the degree of saturation, and $A_1$ is the m.m.f. of the stator current $I_1$. That is, the resultant mutual field is that due to a m.m.f. which has two components:

(1) A "rotating" m.m.f. of constant amplitude $A_1 \sin \beta$, which is directed along the brush axis when the stator current is zero.

(2) A pulsating m.m.f. directed along the brush axis of value $A_1 \sin \beta \left(\frac{n}{n_s} - 1\right)$, which is a maximum when the stator current is zero.

The resultant of these two components is a "rotating" m.m.f. whose value pulsates between $A_1 \sin \beta$ and $\frac{n}{n_s} A_1 \sin \beta$. Owing to saturation, the flux produced by this m.m.f. will have a relatively smaller pulsation. The mean amplitude of the flux will depend both on the speed and on the degree of saturation, and hence the reactances will also depend to some extent on the speed. To retain simplicity, it is necessary to ignore this effect and to assume that the mean value of the flux is that due to a m.m.f. equal to $A_1 \sin \beta$ at all speeds.

The $X_1$ on $I_1$ and $X_{12}$ on $I_1$ curves plotted from the results of the measurement of $X_1$ and $X_{12}$ give the reactances for a given value of $I_1$ when the resultant m.m.f. was equal to $A_1$. When the motor is operating with a current $I_1$ the resultant m.m.f. is roughly $A_1 \sin \beta$, and since $A_1$ is proportional to $I_1$ it follows that the average flux corresponds to that caused by a current $I_1 \sin \beta$ in the stator, with the rotor open-circuited. That is, the values of $X_1$ and $X_{12}$ under running conditions are those corresponding to a current $I_1 \sin \beta$ on the $X_1$ on $I_1$ and $X_{12}$ on $I_1$ curves.

The value of $X_2$ for a given stator current $I_1$ and brush angle $\beta$ is that corresponding to a rotor current

$$I_2 = I_1 \frac{N_1}{N_2} \sin \beta = I_1 \frac{X_1}{X_{12}} \sin \beta$$

on the graph of $X_2$ on $I_2$.

10. *To Measure $R_e$ and $X_e$*

These quantities, on which depend the effect of the shorted coils, can be measured approximately as follows.

(1) With the brushes lifted, measure the stator resistance $R_1$ and $X_1$ with alternating current.

(2) With $\beta = \frac{1}{2}\pi$ and the brushes lowered, the rotor stationary, and shorting lead open, measure the stator resistance and reactance again; let these new values be $R_1'$ and $X_1'$. Then, for a given current $I_1$, neglecting the change in reactance owing to the saturation in Case (1) being slightly different from that in Case (2), we have:

$$R_e = R_1' - R_1, \qquad X_e = X_1 - X_1' \tag{51}$$

where $X_1$, $X_1'$, etc., correspond to a current $I_1 \sin \beta$.

11. *Effect of the Assumption that the Field-form is Sinusoidal*

The above theory is based on the assumption that the field-forms of both stator and rotor are sinusoidal. Actually, the distribution of conductors in a repulsion motor is that shown in Fig. 8, and results in a trapezoidal field-form for the stator and a triangular field-form for the rotor.

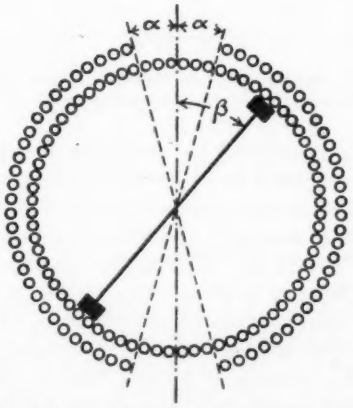


FIG. 8. *Arrangement of windings in repulsion motor. The axis of the stator winding bisects the angle $2\alpha$.*

Various workers, such as Punga (2) and Wall (4–8), have examined the effect of the distribution of the windings on the operation of the motor. Such a procedure leads to the result that the rotational e.m.f. in the rotor, and the mutually induced e.m.f's in stator and rotor, are no longer simple sine and cosine functions of the brush angle $\beta$. Wall has shown that, for a given maximum flux-density and unsaturated iron, and for values of $\beta$ greater than $\alpha$:

(1) The transformer e.m.f. in the rotor due to the stator current is proportional to

$$\theta_c = [\pi - 2\beta]\left[\frac{\pi^2 + 2\pi\beta - 2\beta^2 - 6\alpha^2}{\pi - 2\alpha}\right], \tag{52}$$

(2) The transformer e.m.f. in the stator due to the rotor current is proportional to

$$\theta_D = \frac{\pi^3/3 - 2\pi\alpha^2 - 2\pi\beta^2 + 4\alpha^2\beta + 4\beta^3/3}{\pi}, \tag{53}$$

(3) The rotational e.m.f. in the rotor is proportional to

$$\theta_E = \left[\frac{\pi\beta - \beta^2 - \alpha^2}{\pi - 2\alpha}\right]. \tag{54}$$

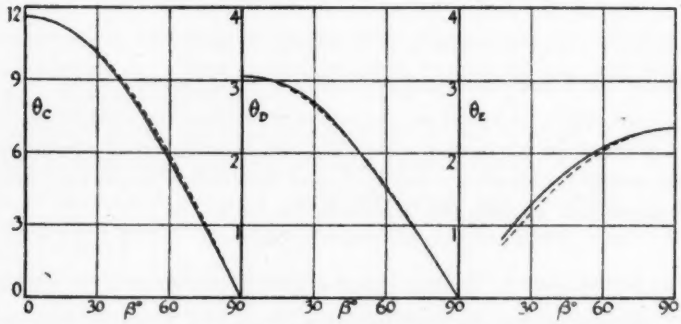


FIG. 9. *Comparison of Wall's functions and sinusoidal curves of same amplitude.* ———, *Wall's functions.* – – – –, *Sine and cosine curves of same amplitude.*

If the field-forms are sinusoidal, the functions $\theta_c$ and $\theta_D$ are proportional to $\cos\beta$, while $\theta_E$ is proportional to $\sin\beta$. Wall gives graphs of these functions for the case $\alpha = 0.1\pi$, which are reproduced in Fig. 9 and compared with cosine and sine functions. It is seen that the difference between the two theories is extremely small for $\theta_c$ and $\theta_D$, whereas in the case of $\theta_E$ (the rotational e.m.f.) the greatest difference is about 9%. In an unsaturated machine it might under certain circumstances be preferable to take the more complex expressions, but since these are based on the assumption of linear relationship between m.m.f. and flux-density it follows that in the actual case, where saturation is present, the above equations do not apply and no advantage is to be expected in using them. The assumption of sinusoidal field-forms, although not strictly rigorous, has the great advantage that the salient features of the motor's operations can be shown by means of comparatively simple formulae.

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## APPENDIX

### Rise and Fall of Current in the Short-circuited Coils

The impedance $Z_s$ of the coils short-circuited by the brushes has been treated as a constant. This is equivalent to the assumption that the circulating currents are fully established at all speeds, whereas in reality as the speed increases the duration of short-circuit decreases, and owing to the time-constant of the shorted coils the circulating currents would be expected to become proportionately smaller. Theoretically, the problem is highly complex, but the simplified theory given below leads to the conclusion that the reduction of the circulating currents due to this effect is not very great.

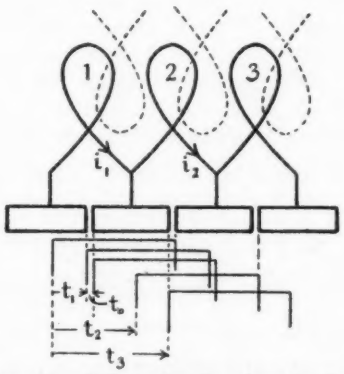


FIG. A1. *Coils undergoing short-circuit.*

Consider three adjacent armature coils, 1, 2, and 3, Fig. A1. In the position shown, coil 1 is short-circuited and the short-circuit of Coil 2 is just beginning. The brush width is taken to be greater than that of one, but less than that of two, commutator segments. Measuring time from the position shown in Fig. A1, the short-circuit of Coil 2 can be divided into five periods:

(1) From $t = 0$ to $t = t_1$, Coils 1 and 2 are both short-circuited.

(2) At time $t_1$ the circulating current $i_1$ in Coil 1 begins to break. It is arbitrarily assumed to fall to zero in a short time $t_0$ at a uniform rate.

(3) From $t_1 + t_0$ to $t_2$ Coil 2 alone carries a circulating current.

(4) At time $t_2$ the short-circuit of Coil 3 begins, and until time $t_3$ Coils 2 and 3 are both short-circuited. Clearly $t_3 - t_2 = t_1$.

(5) At time $t_3$ the short-circuit of Coil 2 is broken, and $i_2$ falls to zero in time $t_0$.

To simplify the analysis, it will be assumed that the resistance of the short-circuit path, $R$, is constant, and that the time of short-circuit is small compared with the period of the a-c. supply. The case where a constant e.m.f., $E$, acts in the shorted coils will therefore be analysed.

Let $L$ be the self-inductance of each coil and $M$ the mutual inductance with adjacent coils. $L$ and $M$ include the mutual effect of the coils short-circuited by the other brushes. It is assumed that the short-circuits under all brushes are synchronized; i.e., that the number of commutator segments is divisible by the number of brush sets. If this is not so, the analysis becomes very complicated.

The circulating currents $i_1$ and $i_2$ are superposed upon the ordinary load currents, which do not enter into the following analysis.

*Interval $t = 0$ to $t_1$.* For the growth of $i_2$ while $i_1$ is flowing:

$$E - L\frac{di_2}{dt} - M\frac{di_1}{dt} = i_2R \tag{1}$$

$$E - L\frac{di_1}{dt} - M\frac{di_2}{dt} = i_1R, \tag{2}$$

whence

$$(L^2 - M^2)\frac{d^2i_2}{dt^2} + 2RL\frac{di_2}{dt} + R^2i_2 = ER, \tag{3}$$

giving

$$i_2 = I - I(Ae^{-Rt/L+M} + Be^{-Rt/L-M}), \tag{4}$$

where $I = E/R$ and $A$ and $B$ are constants. Since $i_2 = 0$ when $t = 0$,

$$A + B = 1. \tag{5}$$

Also

$$i_1 = I - I(Ae^{-Rt/L+M} - Be^{-Rt/L-M}) \tag{6}$$

*Interval $t_0$ ($i_1$ breaks).* At $t_1$, the instant of break, let $i_1 = I'$ while the value of $i_2$ is

$$i_2' = I(1 - Ae^{-Rt_1/L+M} - Be^{-Rt_1/L-M}) \tag{7}$$

$I'$ is assumed to fall to zero at a uniform rate in time $t_0$, so that during this interval

$$i_2 = I + \frac{MI'}{Rt_0} + Ce^{-Rt/L},$$

where $C$ is a constant.

When $t = t_1$, $i_2 = i_2'$, which gives $C$. Thence we find that, when $t = t_1 + t_0$, $i_2$ has the value

$$i_2'' = I + \frac{MI'}{Rt_0}[1 - e^{-Rt_0/L}] - Ie^{-Rt_0/L}[Ae^{-Rt_1/L+M} + Be^{-Rt_1/L-M}]. \tag{8}$$

We may legitimately put $t_0 \ll L/R$, so that the second term becomes very closely equal to $MI'/L$, and in the third term $e^{-Rt_0/L} \doteq 1$. Hence

$$i_2'' \doteq i_2' + MI'/L. \tag{9}$$

*Interval $t = t_1 + t_0$ to $t_2$.* During this interval the current $i_2$ flows unaccompanied by any circulating current in Coils 1 or 3, so that $i_2 = I + De^{-Rt/L}$. Putting $i_2 = i_2''$ when $t = t_1 + t_0$ we find

$$i_2 = I - [I - i_2' - MI'/L]e^{-R(t-t_1-t_0)/L}. \tag{10}$$

*Interval $t_2$ to $t_3$.* At time $t_2$, Coil 3 begins its short circuit, so that the equation for $i_2$ must now have the same form as Equation (6), for during this interval $i_2$ must be identical with $i_1$ during the first interval $t_1$. That is:

$$i_2 = I - I[Ae^{-R(t-t_2)/L+M} - Be^{-R(t-t_2)/L-M}]. \qquad (11)$$

But when $t = t_2$, $i_2$ must be given both by Equations (10) and (11). Whence, putting $B = 1 - A$ and $t_2 - t_1 - t_0 = t_s$, we find for the constants $A$ and $B$:

$$A = \frac{1 + e^{-Rt_s/L}(e^{-Rt_1/L-M} - MI'/LI)}{2 - e^{-Rt_s/L}(e^{-Rt_1/L+M} - e^{-Rt_1/L-M})} \qquad (12)$$

$$B = \frac{1 - e^{-Rt_s/L}(e^{-Rt_1/L+M} - MI'/LI)}{2 - e^{-Rt_s/L}(e^{-Rt_1/L+M} - e^{-Rt_1/L-M})}. \qquad (13)$$

At time $t_3$ (where $t_3 - t_2 = t_1$) the short-circuit of Coil 2 begins to break, and at this instant $i_2$ must be equal to $I'$. Whence it is found that

$$\frac{I'}{I} = \frac{2 - (e^{-Rt_1/L+M} - e^{-Rt_1/L-M})(e^{-Rt_s/L} + 1) - 2e^{-Rt_s/L}\, e^{\frac{-Rt_1}{L-M}}\, e^{\frac{-Rt_1}{L+M}}}{2 - e^{-Rt_s/L}\left[\left(1 + \frac{M}{L}\right)e^{-Rt_1/L+M} - \left(1 - \frac{M}{L}\right)e^{-Rt_1/L-M}\right]}. \qquad (14)$$

Substitution for $I'/I$ in Equations (12) and (13) gives the final values of $A$ and $B$, but the expressions are too unwieldy to be written down here in symbols. The best way to proceed is to take a typical numerical case. The repulsion motor cited in the paper had 48 segments. Thus at 2400 r.p.m. ($n_s = 1800$), $t_s = 5.2 \times 10^{-4}$ sec. ($1/f = 1.67 \times 10^{-2}$ sec.). Suppose the brush width is 1.5 times the width of a segment. Then $t_1 \doteq 2.6 \times 10^{-4}$ and $t_s \doteq 2.6 \times 10^{-4}$. If $L - M$ is 3% of $L$: $L = 7.6 \times 10^{-4}$, $L + M = 1.5 \times 10^{-3}$, $L - M = 2.3 \times 10^{-5}$; $R = 0.5$; $M/L = 0.97$. Then

$$e^{-Rt_s/L} = 0.8428; \quad e^{-Rt_1/L+M} = 0.917; \quad e^{-Rt_1/L-M} = 0.00352.$$

Substituting these values in Equation (14), we get $I'/I = 0.6511$, whence from Equations (12) and (13):

$$A = 0.3826 \qquad B = 0.6174, \qquad \text{so that}$$

*From $t = 0$ to $t = t_1$ (Equation (4)):*

$$i_2 = I[1 - 0.3826\, e^{-Rt/L+M} - 0.6174\, e^{-Rt/L-M}].$$

*At $t_1$ (Equation 7):*

$$i_2' = 0.6470\, I.$$

*At $t_1 + t_0$ (Equation 9):*

$$i_2'' = 1.2786\, I.$$

*From $t_1 + t_0$ to $t_2$:*

$$i_2 = I[1 + 0.2786\, e^{-R(t-t_1-t_0)/L}],$$

*so that at $t_2$ ($t_2 - t_1 - t_0 = t_s$):*

$$i_2''' = 1.2348\, I.$$

*From $t_2$ to $t_3$:*

$$i_2 = I - I[0.3826\, e^{-R(t-t_2)/L+M} - 0.6174\, e^{-R(t-t_2)/L-M}],$$

*and at $t_3$:*

$$i_2'''' = 0.6511\, I = I'.$$

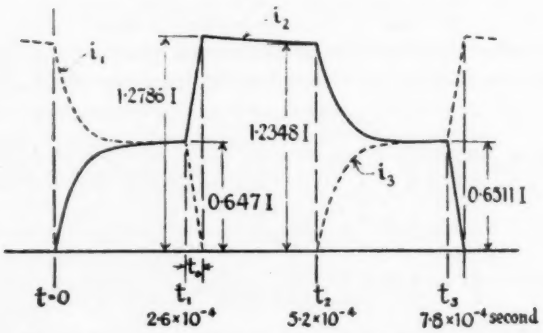


FIG. A2. *Wave forms of currents in coils short-circuited by a brush.*

The three time constants are:

$L/R = 1.52 \times 10^{-3}$, $(L - M)/R = 4.6 \times 10^{-5}$, $(L + M)/R = 3 \times 10^{-3}$

The theoretical wave-form of $i_2$ is shown in Fig. A.2. The average magnetizing effect of the circulating currents is that due to $i_1 + i_2 + i_3$. This has an average value of 1.2616 $I$. If the currents were fully established in each short-circuited coil during the whole period of short-circuit, the average circulating current would be 1.5 $I$. Thus in this particular case the circulating currents at 2400 r.p.m. (133% of synchronous speed) have a value only 16% less than if they were full established. Repeating the calculations for 600 and 1200 r.p.m. (one-third and two-thirds of synchronous speed), we find the decrease to be:

600 r.p.m.: 11.9% decrease
1200 r.p.m.: 13.5% decrease.

It therefore appears to be justifiable to treat $Z_s$, to a first approximation, as a constant.

## NOTE

From Equation (30) it is seen that the rotational e.m.f. $E_{r1} = \frac{n}{n_s} X_{rm} I_s$ is proportional to $\frac{n}{n_s}\left(1 - \frac{n^2}{n_s^2}\right)$, and if included results in great complication. Fortunately the effect is zero both at standstill and at synchronism, and is small at intermediate speeds. Since repulsion motors are not usually designed to run at speeds much above synchronism, this effect is neglected in comparison with $E_{s1}$. Thus no error is introduced in the results for the starting conditions, which are affected profoundly by the transformer e.m.f. $E_{s1}$, and very little error over the normal speed range of the motor. This approximation has the great advantage of enabling us to retain the practicability of a graphical construction, which is so valuable in giving a general picture of the behaviour of a machine. For accurate design work, the effect can be included, and the reader is referred to a recent paper by P. H. Trickey (Trans., Am. Inst. Elect. Engrs. 60(2) : 67-72. 1941.)

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## NOTE ON THE PYROLYSIS OF METHYL AND ETHYL CYANIDES[1]


BY B. S. RABINOVITCH[2] AND C. A. WINKLER[3]



### Abstract

The products of pyrolysis of methyl and ethyl cyanides at 865° and 675° C. respectively have been determined at each of two flow rates. From methyl cyanide were obtained hydrogen, methane, hydrogen cyanide, and carbon. Small amounts of "$C_2$" hydrocarbons and high boiling materials were also formed. The results indicate that hydrogen cyanide is a primary product.

Ethyl cyanide yielded hydrogen, methane, ethane, ethylene, hydrogen cyanide, methyl cyanide, acrylonitrile, and carbon, together with small amounts of succinonitrile and higher boiling materials. The reaction is obviously complicated by secondary changes.


A kinetic study of the thermal decomposition of the lower aliphatic nitriles has been contemplated as part of a series of investigations into nitrile reactions. Although the catalytic cracking of higher fatty acid nitriles has been the subject of industrial research (5), no information about the thermal decomposition of the short chain members is reported. Therefore, before attempting a kinetic investigation, the pyrolysis of methyl and ethyl cyanides has been studied at different flow rates to obtain information about the nature of the reactions involved and the products formed.

### Materials and Procedure

The nitriles were obtained commercially and purified by distillation. The materials used boiled over a range of 0.2° C.

Pyrolysis was effected in a silica tube, 55 cm. in length and 2 cm. in diameter, wound with a heating element and suitably insulated. Temperature was controlled manually and measured with a chromel-alumel thermocouple inserted at one end. Temperature variation along the tube was 10° C. Approximately 45 gm. of nitrile was injected into the furnace by mercury displacement from a burette. The tube was connected through graded seals to a series of traps maintained at temperatures of 100°, 0°, −78°, and −183° C. Liquid products were collected at 0° and 100° C., and gases condensed in the colder traps, or if not condensed, were bled off into evacuated flasks. A


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constant operating pressure was thus maintained during an experiment. Experiments were made at two flow rates with each cyanide.

Gaseous products were analysed in a low-temperature still of the Podbelniak type, and liquid products were determined by distillation on a Whitmore column. In most instances, the identity of the products was verified by confirmatory tests.

## Results

The results are shown in Table I.

TABLE I

PYROLYSIS AND ANALYTICAL DATA

| Pyrolysis data | Ethyl cyanide at 675° C. | | Methyl cyanide at 865° C. | |
|---|---|---|---|---|
| Flow rate, cc. liq./min. | 1.0 | 0.22 | 0.80 | 0.23 |
| Operating press., cm. Hg. | 60 | 45 | 52 | 35 |
| Percentage decomposed | 64.5 | 98.5 | 48.4 | 94.6 |
| Products | Moles/mole cyanide decomposed | | Moles/mole cyanide decomposed | |
| $H_2$ | 0.24 | 0.32 | 0.24 | 0.99 |
| $CH_4$ | 0.15 | 0.43 | 0.39 | 0.23 |
| $C_2H_4$ | 0.18 | 0.032 | | |
| $C_2H_2 + C_3H_4$ | | | 0.043 | 0.012 |
| $C_2H_6$ | 0.14 | 0.13 | | |
| HCN | 0.42 | 0.79 | 0.85 | 0.86 |
| $CH_3CN$ | 0.27 | 0.084 | | |
| $CH_2{=}CHCN$ | 0.24 | 0.10 | | |
| $(CH_2CN)_2$ | 0.024 | 0.024 | | |
| Higher boiling products | 0.9* | 0.7* | 0.8* | 0.4* |
| Carbon | 1.8*† | 5.8*† | 3.4*† | 6.2*† |
| Tar | | | 0.7* | 0.3* |

* *Recorded in grams.*

† *A deposit of carbon was formed over the walls of the connecting tubing, and its estimation was difficult.*

The gaseous products from the methyl cyanide decomposition are hydrogen, methane, and small amounts of "$C_2$" unsaturated hydrocarbons. Their identities were confirmed by the usual combustion and absorption methods. Cyanogen was not found, either by distillation, or by methods outlined by Dennis (1).

In the liquid products from methyl cyanide, hydrogen cyanide (b.p. 26° C.) was identified by a boiling point of 25 to 27° C., and by formation of a white precipitate with silver nitrate. The small amount of higher boiling material was a light yellow liquid with the odour of benzonitrile. The liquid thickened and turned reddish-brown on standing.

The identities of the gaseous products from the ethyl cyanide decomposition —hydrogen, methane, ethylene, and ethane—were confirmed, again by combustion or absorption after the distillation.

The liquid products obtained from ethyl cyanide were separated into three fractions. One of these was identified as hydrogen cyanide from its boiling point and by silver nitrate precipitation. A second fraction had a boiling range from 75 to 84° C. Possible products boiling in this range are benzene (b.p. 80° C.), methyl cyanide (b.p. 81 to 82° C.), acrylonitrile (b.p. 78 to 79° C.) and ethyl isocyanide (b.p. 80° C.). The characteristic odour of ethyl isocyanide was absent, and the oxalic acid test and the hydrolysis analysis method of Guillemard (3) did not indicate its presence. Bromine was rapidly absorbed by the liquid mixture, however, and a bromide was prepared according to the method of Moureu (4) for acrylonitrile. Its boiling point was 125 to 132° C. at 58 mm., and its density 2.13 at 25° C. These identify it as the dibromide of acrylonitrile, with b.p. 126 to 129° C. at 55 mm. and density 2.16 at 0° C. The nitrilic character of the remaining portion of the fraction (methyl cyanide) was verified by hydrolysis, with production of an equivalent of ammonia.

The third fraction of the ethyl cyanide liquid products had a boiling range of 105 to 200° C. at 20 mm. Fractional distillation yielded a white solid of m.p. 50 to 51° C., which is in agreement with the melting point of 54.5° C. for succinonitrile; the boiling point of succinonitrile is 159° C. at 20 mm., which falls within the range of the third fraction. The remainder of the fraction was liquid at room temperature and probably contained other dinitriles. These might be $CH_2(CN)_2$, $(CH_2)_3(CN)_2$ and $(CH_2)_4(CN)_2$, which are liquids around room temperature and boil at temperatures throughout the range found. Traces of benzonitrile were also indicated by the characteristic odour.

## Discussion

The thermal decomposition of methyl cyanide appears to proceed in a relatively simple manner. Hydrogen cyanide occurs in amounts substantially equivalent to methyl cyanide disappearance and apparently is a primary product. Hydrogen is produced to some extent at least by secondary reaction. The increases (with time) in the proportion of hydrogen and of "$C_2$" hydrocarbons can both be attributed to the decomposition of methane (6). Carbon is formed in large amounts, probably as a result of hydrocarbon decomposition and other cracking reactions at the high temperature employed.

The decomposition of ethyl cyanide is evidently very complex. Formation of hydrogen, methane, hydrogen cyanide, and carbon is partially due to secondary reactions; increase in their relative proportions with time is presumably due to partial decomposition of ethylene (6) and nitrilic products. Decomposition at 675° C. of the methyl cyanide formed possibly occurs as a result of sensitization by free radicals. Dehydrogenation of ethyl cyanide would account for the formation of acrylonitrile; the catalytic dehydrogenation of ethyl cyanide has been reported (2).

The ethyl cyanide decomposition does not appear suitable for kinetic study even at the lowest temperature (590° C.) at which decomposition is conveniently measurable. A kinetic study of the thermal decomposition of methyl cyanide in a temperature region around 800° C. is in progress.

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# THE HYDROLYSIS OF ACID AMIDES IN CONCENTRATED HYDROCHLORIC ACID SOLUTIONS[1]

By B. S. Rabinovitch[2] and C. A. Winkler[3]

## Abstract

The Arrhenius constants have been evaluated for the hydrolysis of formamide, acetamide, propionamide, and benzamide in hydrochloric acid solutions over the concentration range 1 to 10 *N*. There is approximate correspondence between reaction rates and activation energies for the series of amides. An increase in observed activation energy with increasing acid concentration was found for all amides. The maximum in rate of hydrolysis, which occurs at higher acid concentrations, is discussed and accounted for by the variation in the Arrhenius constants with acid concentration.

## Introduction

The relations between reaction rate in solutions of electrolytes and such factors as concentration of electrolyte, mean ion activity, and the primary salt effect, have frequently been examined and discussed without regard to possible changes in the parameters $A$ and $E$ of the Arrhenius equation over the range of concentrations considered. While this may often be valid for dilute solutions, particularly for reactions of zero ionic type (2, 18), recent work on ionic reactions in dilute solution has shown the dependence of $A$ and $E$ on ionic strength and dielectric constant (27, 40). Similarly, the salt effect in such reactions has been shown to be related to changes in the Arrhenius constants (28, 29).

Little study has been made of the parameters of the Arrhenius equation for concentrated solutions of electrolytes. Here, the situation is more complicated. The consideration of the dependence of reaction rate on acid concentration necessarily involves the simultaneous variation of dielectric constant and composition of the medium. Other factors in addition to those present in dilute solution may also operate. v. Kiss and co-workers (22), in studies of the neutral salt effect in ionic reactions at high salt concentrations, have found that changes in the Arrhenius constants with salt concentration may occur. Leininger and Kilpatrick have recently found a change in the observed activation energy with change of acid concentration for hydrolysis of sucrose (25) and ethylal (26) in concentrated acid solutions, a behaviour they believe general for reactions in concentrated solutions of electrolytes. Where variation of the Arrhenius constants does occur, their determination over the range of acid concentration under consideration is obviously important, since in the absence of this information undue emphasis may be placed on less relevant factors in the interpretation of the rate of reaction.

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Of the many reactions that might have been studied to obtain additional information on the changes in $A$ and $E$ with acid concentration, the hydrolysis of amides and nitriles in concentrated acids appeared of particular interest. Both reactions are of the zero ionic type, of which many studies have been made at a single temperature in dilute and concentrated acid solutions. Some determinations of activation energy for amide and nitrile hydrolysis have been made, but these usually refer to dilute solutions and appear in some instances to be rather unreliable. A fact of more interest, however, is that the effect of acid concentration on rate of hydrolysis is quite different for the two reactions. With amides, the unimolecular velocity constants increase slowly with acid concentration and pass through a maximum value at various acid concentrations from 3 to 6 $N$ (23), depending on the amide concerned. The rate of nitrile hydrolysis, on the other hand, apparently increases continuously and more rapidly with acid concentration than any other reaction studied over a similar concentration range (24).

The purpose of the present paper is to present the results of an investigation on the hydrolysis of formamide, acetamide, propionamide, and benzamide in concentrated hydrochloric acid. The results for nitriles will be presented in a later paper.

## Materials and Procedure

Formamide was obtained commercially and purified by repeated distillation *in vacuo*. Though traces of ammonium formate and water persist after such treatment (39), these should have no appreciable effect on the rate of hydrolysis. Solutions were stored at 0° C. after standardization and determination of the free ammonia content.

Acetamide, propionamide, and benzamide were also obtained commercially and purified by recrystallization. Their solutions were prepared directly by weight. The amide normalities in the various reaction mixtures were as follows:

| Acid normality | 1.00 | 4.00 | 6.48 | 8.47 | 10.13 |
|---|---|---|---|---|---|
| Formamide | 0.3971 | 0.3929 | | 0.3940 | |
| Acetamide | 0.2039 | 0.2045 | | 0.2032 | |
| Propionamide | 0.2025 | 0.2031 | 0.2033 | 0.1982 | 0.1991 |
| Benzamide | 0.0996 | 0.0998 | | 0.04987 | |

Reagent grade hydrochloric acid was standardized by density determinations and by titration, and diluted to the required concentrations.

For experiments near room temperature, reaction solutions were prepared by mixing appropriate volumes of amide and acid solutions at 0° C. in stoppered, Pyrex reaction vessels. At higher temperatures, reaction took place in sealed Pyrex bulbs. In both cases, dead space was negligible. The reaction vessels were immediately immersed in thermostats regulated to within 0.1° C.,

temperatures being determined with standard thermometers. A correction, found experimentally, was made for the time required for solutions to reach the reaction temperature. For experiments below room temperature, the reactants were brought to the desired temperature before being mixed in the reaction vessel. Concentrations after mixing were calculated from density–composition data for hydrochloric acid (International Critical Tables). For this purpose, the dilute amide solutions were treated as pure water. Since the hydrolysis of amides yields ammonia and the corresponding acid, the course of the reaction, except with formamide, was followed by analysis for ammonia by Folin's aspiration method (15), calibrated and used at 0° C. A small correction, evaluated experimentally, was applied for the hydrolysis of unconverted amide during analysis. With formamide, this method caused decomposition of the unconverted amide and it was therefore replaced by the formol titration method for ammonia (19, p. 525).

## Results

The unimolecular velocity constants obtained at different acid concentrations and temperatures for the four amides used are given in Table I. Each constant is the mean of five or six individual values that usually deviated from the recorded value by not more than 3%. No correction has been applied for concentration taken as at 25° C., nor for variation of collision number with temperature. These errors partially cancel each other, and should have negligible influence for comparison of activation energies at different acid concentrations. Comparison of the rate data with those available in the literature is difficult, extrapolation or interpolation usually being necessary. The general agreement is within experimental error. For comparative purposes within the present study, any systematic errors in rate determinations should largely cancel.

The values of $A$ and $E$ at different acid concentrations, for each amide, have been calculated from the Arrhenius relation: $k = Ae^{-E/RT}$. The equation appeared to be satisfactorily obeyed in all cases. In evaluating a bimolecular value of log $A$, which is included for purposes of illustration in later discussion, the velocity constants, expressed in seconds, were divided by acid normality. The results of these calculations are given in Table II, together with values obtained directly or calculated from the data of other workers. In a number of these investigations, the erroneous procedure has been followed of expressing the results as a temperature coefficient, which is obviously temperature dependent, and using the value so obtained for discussion and for comparison with data obtained at different temperatures.

It is evident from Table II that the activation energies increase with acid concentration. The changes with formamide and benzamide are only about 1000 cal. for the whole concentration range, but consideration of the plots of log $k$ against temperature shows that the relative values are less than 500 cal. in error. The fact that the changes for these two amides are in the

TABLE I

VELOCITY CONSTANTS FOR THE HYDROLYSIS OF AMIDES WITH HYDROCHLORIC ACID

| Temp., °C. | $k \times 10^5$ hr.$^{-1}$ | | | | |
|---|---|---|---|---|---|
| | Concentration of acid, normality | | | | |
| | 1.00* | 4.00 | 6.48 | 8.47 | 10.13 |
| **Formamide** | | | | | |
| 0.0 | 2.84 | 10.7 | | 5.30 | |
| 14.8 | | 60.3 | | | |
| 19.8 | 28.5 | 99.4 | | 57.5 | |
| 24.7 | 49.2 | 178. | | 102. | |
| 29.4 | 77.1 | | | 161. | |
| **Acetamide** | | | | | |
| 40.6 | 13.2 | 16.9 | | 4.02 | |
| 45.7 | 20.6 | 29.4 | | | |
| 51.9 | | 50.6 | | | |
| 52.0 | | | | 12.8 | |
| 59.6 | 71.4 | 107. | | 26.9 | |
| 70.7 | 183. | | | 80.0 | |
| **Propionamide** | | | | | |
| 29.0 | | 9.01 | | | |
| 29.5 | 5.78 | | 4.62 | | |
| 40.5 | 16.4 | 29.4 | 13.2 | 5.88 | 3.17 |
| 49.9 | | 74.7 | | | |
| 50.1 | 39.6 | | 36.0 | 17.0 | 8.87 |
| 59.6 | 95.8 | 170. | 83.8 | 41.9 | 22.6 |
| 69.6 | | | | 95.5 | |
| 70.8 | | | | | 66.6 |
| **Benzamide** | | | | | |
| 48.7 | | 3.55 | | 1.73 | |
| 59.6 | 3.44 | 11.0 | | 5.58 | |
| 68.7 | 8.59 | 27.0 | | 13.9 | |
| 78.6 | 18.7 | 63.8 | | 34.3 | |
| 89.6 | 52.9 | | | | |

* *At this concentration, a downward drift in velocity constants, due to depletion of the catalyst by ammonia formation, occurs; the bimolecular constants are satisfactory.*

same direction as the larger increases observed for acetamide and propionamide also indicates that the observed $E$ changes are significant.

The variation of the values of log $A$ with acid concentration appears to be similar for all amides. For a given amide, the unimolecular log $A$ values increase with increase in $E$, as is commonly observed. The bimolecular values (Column 3, Table II) increase from 1 to 4 $N$ and then tend to remain constant or decrease at higher acid concentrations. However, since the total variation of log $A$ is small, and since it is uncertain whether normality is the proper function of acid concentration by which $k$ should be divided, stress is not placed on this behaviour.

TABLE II

ARRHENIUS CONSTANTS FOR EACH AMIDE AT VARIOUS HYDROCHLORIC ACID CONCENTRATIONS

| Amide | Acid concentration, normality | Log $A$ | | $E$, cal. | | Remarks |
|---|---|---|---|---|---|---|
| | | Based on $k/N$ | Based on $k$ | This investigation | Previous investigations | |
| Formamide | 1.00 | 9.6 | 9.6 | 18,400 | 19,100[1] | [1] Crocker (9). A systematic difference exists between the present results and those of Crocker, which are invariably higher. Kilpi (21) has noted some discrepancies between his velocity constants and those of Crocker. It may be that some systematic error has entered into the latter's results, which otherwise appear to be of good precision. |
| | 4.00 | 9.7 | 10.3 | 18,500 | | |
| | 8.47 | 9.7 | 10.6 | 19,300 | | |
| Acetamide | 1.00 | 8.7 | 8.7 | 18,800 | 20,780[1] | |
| | | | | | 15,900[2]* | |
| | | | | | 18,800[3] | |
| | | | | | 15,500[4]* | |
| | 4.00 | 9.0 | 9.6 | 20,000 | 20,600[2]* | |
| | 5.00 | | | | 21,000[5]* | |
| | 8.47 | 8.9 | 9.8 | 21,200 | | |
| Propionamide | 1.00 | 8.6 | 8.6 | 18,600 | 19,830[1] | [2] Euler and Rudberg (14). The average error in the velocity constants used was as high as 15%. Acid concentration was approximately 0.1 $N$. |
| | | | | | 14,400[4]* | |
| | 4.00 | 8.8 | 9.4 | 19,400 | | |
| | 6.48 | 8.5 | 9.3 | 19,700 | | |
| | 8.47 | 8.4 | 9.3 | 20,200 | | |
| | 10.13 | 8.8 | 9.8 | 21,300 | | |
| Benzamide | 1.00 | 9.2 | 9.2 | 21,700 | | [3] Moelwyn-Hughes (32, p. 245). Calculated from the results of several workers at about 1 $N$ acid. |
| | 4.00 | 9.3 | 9.9 | 21,900 | | |
| | 8.47 | 9.1 | 10.0 | 22,600 | | [4] v. Peskoff and Meyer (34) |
| | | | | | | [5] Taylor (38) |

* *Based on two temperatures only.*

## Discussion

The acid catalyzed hydrolysis of amides has usually been interpreted on the basis of Euler's theory of interacting ions (11, 12, 13). While the theory is useful for discussion of certain reactions, there have been serious objections to its general validity (6). As applied to the acid catalyzed hydrolysis of amides, where amide cation is considered the reacting species, the equilibrium formation of the cation may instead be considered as a preliminary step in the formation of an activated intermediate. This viewpoint renders unnecessary the improbable assumptions of Euler concerning the activation of the cation.

The maximum in the rate of hydrolysis, as given by the unimolecular velocity constants, was first observed for acetamide (5) and has been shown to be general for the acid catalyzed hydrolysis of amides (23). This maximum has usually been interpreted as being due to the occurrence of a maximum concentration of an amide cation at a certain acid concentration (5, 13, 23, 36). With different amides and a given acid, or with different acids and a given amide, the acid concentration at the maximum might be expected to have different values, and this is, in fact, the observed behaviour.

There is considerable disagreement concerning the structure of the cation. However, the imide structure seems to be favoured in some recent kinetic work (23, 35). Some of the data from dipole moments and absorption spectra measurements indicate that amides exist mainly in the imide form in aqueous solution (3). The fact that disubstituted amides, $CH_3CONR_2$, for which the imide structure is not possible, are hydrolyzed very slowly, as indicated by qualitative examination (1, 31), would also seem to suggest that the reactive cation is of the imide form.

The decrease in hydrolysis rate following attainment of the maximum has been variously explained. It has been suggested that at higher acid concentrations an unreactive, undissociated salt is formed (5, 13). In opposition to this, it has been pointed out that the acid concentration corresponding to the maximum should depend on amide concentration, and it is stated that this is not in agreement with experiment (23). This criterion of undissociated salt formation does not take into account possible complications arising from change in degree of dissociation of the amide with change of amide concentration. More data would seem necessary to check these points. It should be borne in mind, moreover, that high amide concentrations might introduce changes arising simply from changes in reaction conditions as non-electrolyte concentration is altered.

The decrease in rate after the maximum has been ascribed by Krieble and Holst (23) to direct proportionality between rate and square of the activity of water, after a maximum constant concentration of cation is reached. However, existing data indicate that the rate constants, at the same acid concentrations, fall off more markedly with acetamide and propionamide than with formamide and, possibly, benzamide, whereas the proportional decrease would be expected to be the same for all amides if decrease in activity of water alone determined the decrease in rate constant. As these authors have pointed out, however, the available rate data at high acid concentrations are scanty and more measurements would be desirable. Alternatively, it has been suggested by the same authors that increased acid concentration might favour the original amide and thus lower the concentration of cation. Relevant to this suggestion, measurements of the base dissociation constants of amides over the range of acid concentrations concerned would be of interest.

The changes in reaction rates with acid concentration may be accounted for by the observed changes in $A$ and $E$ (Table II). In terms of the unimolecular constants, the rates pass through a maximum in the region of acid concentrations of 3 to 6 $N$, while on the basis of the bimolecular constants they show steady decrease with increasing acid concentrations. If the reaction proceeds by way of an equilibrium cation, the unimolecular constants should reach, but not pass through, a maximum. This behaviour corresponds to a dominant effect of $E$ change, since, while $E$ increases for all the amides, the $A$ values, corresponding to unimolecular or bimolecular constants, either increase more slowly than $E$ or pass through a maximum at higher acid concentration.

The influence of the nature of the amide on the rate of hydrolysis is indicated in Fig. 1. Obviously there is approximate correspondence between rate and activation energy, at each of the several acid concentrations. Defect from exact linearity can be attributed to simultaneous variations in energy and entropy of activation. This behaviour is commonly observed for aliphatic compounds, where, as in the present instance, the substituent is close to the reacting group (20, 41). It would be interesting to study meta- and para-substituted amides, since with these derivatives only minor variations in entropy of activation occur (16, pp. 121, 208, 244).

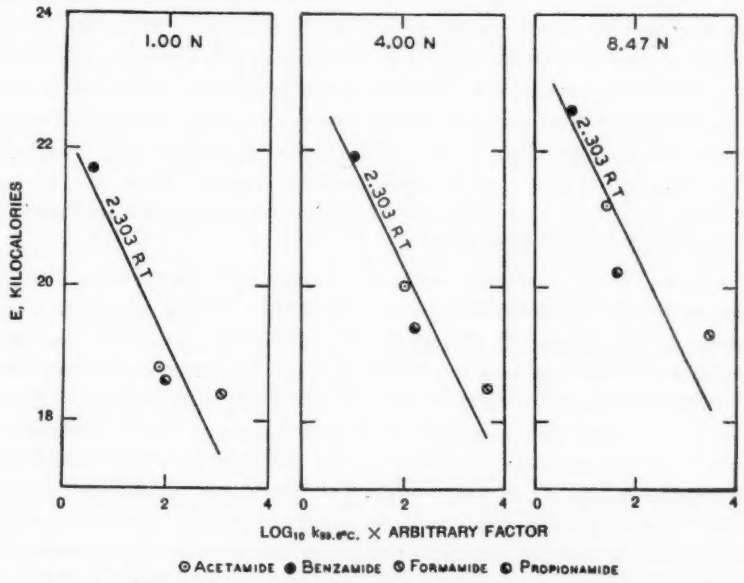


FIG. 1. *Plot of log k against E for different amides at three acid concentrations.*

Proportionality between the rate constants for different amides and the dissociation constant of the corresponding carboxylic acids has been suggested by Crocker (9) for the acid catalyzed hydrolysis, and by Calvet (7) for the alkaline hydrolysis of amides. Hammett (16, pp. 121, 208, 244) has pointed out, however, that in general, linear free energy relations do not apply to reactions of aliphatic compounds where variation of structure from member to member of a series causes variation in entropy of activation. For the acid hydrolysis of aliphatic amides, there is not even qualitative dependence of rate constants on dissociation constants of the acids. For example, the rate of hydrolysis of propionamide is greater than that of acetamide, although the dissociation constant of propionic acid is smaller than that of acetic acid. The relations are also inverted for benzamide relative to acetamide or propionamide.

The magnitude of the $A$ factor (Table II) places the acid catalyzed hydrolysis of amides in the category of "slow" reactions, as previously pointed out by Christiansen (8). Reactions involving ions generally have "normal" rates in aqueous solution (33). The relative slowness of amide hydrolysis might be due to the fact that if the reacting species is the amide cation, the concentration of which is appreciably lower than the amide concentration in dilute solution (13), the calculated velocity constants will be lower than the true values. The cation concentration increases with acid concentration, however, and it might be expected that at high acid concentrations the rate would become more nearly normal. The observed $A$ values do actually increase with acid concentration (Table II, Column 4). However, since $E$ increases, and parallel variation of $A$ and $E$ is commonly observed, the increase in $A$ cannot here constitute a criterion of the validity of this explanation.

It is interesting to note that if the reaction is treated on the basis of ternary collisions, normal $A$ values result (33) and the magnitude and direction of changes in $E$ with acid concentration may be altered. However, viscosity data for hydrochloric acid solutions are not extensive and this treatment has not been applied to the present data.

The change in the Arrhenius activation energy with change of acid concentration is specific for different amides (Table II). It might be that a small temperature dependence of $A$ and $E$ would suffice to make the observed $E$ values deviate from the true (4). Moreover, if the temperature dependence of $E$ varies with concentration of acid, the deviation from the true value will similarly vary, and the observed values will apparently vary with concentration. Hydrolysis reactions are of a type that are known to exhibit temperature dependence of $E$ (30). Moreover, there are indications that such an effect exists in the alkaline hydrolysis of amides (10, 30). It is not possible, from the data of this investigation, to exclude temperature dependence of the Arrhenius constants. Very accurate measurements are necessary to determine the magnitude of the temperature coefficient of $E$, since it is often very small. However, no indication of an $E$ change with temperature has been given by the work of Crocker (9), the precision of which appears to be of the requisite order. Furthermore, the variations in $A$ and $E$, if they do occur, usually tend to cancel each other. The correspondence between change of rate and change of $E$ also indicates that the $E$ change is fundamental.

It is probable that changes in $E$ depend simply upon variation of reaction conditions, but it might be that there is a change in mechanism as acid concentration is altered. Euler and Ölander (13) have indicated that complexity may attach to the mechanism for the hydrolysis of acetamide at higher acid concentrations. It may be noted that hydrolysis of amides does not give the theoretical relation between rate constant and acidity function of Hammett required for specific hydrogen ion catalysis (23). This is of particular interest, since Euler's theory, does, in part, form the basis of Hammett's treatment (17).

This might indicate that mechanisms other than that involving the equilibrium formation of an amide cation may occur. However, the failure is not conclusive, since Hammett's assumptions might not be fulfilled here (42). The work of Reitz (36) on the heavy water hydrolysis indicates specific hydrogen ion catalysis, although objection to the Bonhoeffer-Reitz criterion has been raised (37).

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# PASTURE STUDIES

## XXIII. A PROPOSED MODIFICATION OF THE FLUORIMETRIC METHOD FOR THE ESTIMATION OF RIBOFLAVIN[1]

By R. A. Chapman[2] and W. D. McFarlane[3]


### Abstract

The fluorimetric method for the determination of riboflavin in foodstuffs has been modified to permit the use of the fluorimeter described by Froman and McFarlane (4). Extracts are prepared by enzymatic digestion and purified by barium chloride precipitation and benzyl alcohol extraction. Photochemical reduction of riboflavin in the 'blank' is effected by stannous chloride in benzyl alcohol solution.


### Introduction

Numerous methods, based on the measurement of the intensity of the yellow-green fluorescent light emitted when the solution is irradiated with light of certain wave-lengths, have been proposed for the determination of riboflavin. The riboflavin has generally been extracted from tissues by means of acetone or methanol and the extract purified by adsorption on Franconite, Floridin earth or lead sulphide, etc. Adsorption effects only a partial removal of substances that interfere with the fluorimetric reading, and further purification is necessary. Emmerie (2) and Conner and Straub (1) employed controlled oxidation with permanganate and hydrogen peroxide. Sullivan and Norris (9) used sodium hydrosulphite and estimated the riboflavin from the difference between the fluorescence readings of the reduced and unreduced samples. Benzyl alcohol was used by Emmerie (3) to separate riboflavin from interfering substances in the extract, Greene and Black (5) having shown it to be the best solvent.

After a careful study of these various methods the writers have developed a simple and rapid modified procedure that omits the adsorption step and employs *(a)* benzyl alcohol as an immiscible solvent for the extraction of riboflavin, *(b)* barium chloride solution for the removal of impurities in the extract, and *(c)* a benzyl alcohol solution of stannous chloride for the preparation of the blank. Since this investigation was completed, Najjar (8) has proposed a procedure using a pyridine–butyl-alcohol mixture as the immiscible solvent. However, the writers have found benzyl alcohol to be quite satisfactory and its use has certain advantages in the particular procedure reported herein.

### Experimental

Acid extraction (1) or extraction with an acid–acetone mixture (9) have been the chief methods proposed for the preparation of a crude extract from tissues. Benzyl alcohol is miscible with acetone, and phosphoric esters of

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[2] *Research Assistant, Macdonald College Pasture Committee.*

[3] *Professor of Chemistry.*

riboflavin are not extracted by benzyl alcohol. Therefore it appeared logical to use pepsin and takadiastase digestion as in the determination of thiamine (7) so that simultaneous estimation of riboflavin and thiamine would also be possible. Pepsin extraction, compared with acid extraction, gave slightly higher and more reproducible results; this confirmed Van Duyne's (10) findings. Incubation at 37° C. must be carried out in a dark cabinet, but no special precautions need be taken to exclude light at any other stage in the determination.

Benzyl alcohol alone formed, with various extracts, heavy emulsions that were very difficult to break. A further disadvantage lay in the fact that the benzyl alcohol, having the greater density, separated as the lower layer along with a certain amount of precipitated material, thus making it necessary to use suction and filtration. These difficulties were overcome by adding a barium chloride solution, which reduced the tendency for emulsions to form, precipitated impurities in the extract, and increased the density of the aqueous phase so that the clear benzyl alcohol extract remained on the top. Zinc acetate is a better precipitant than barium chloride, but it is appreciably soluble in benzyl alcohol and forms a cloudy precipitate with stannous chloride.

For the preparation of the blank, a benzyl alcohol solution of stannous chloride was found to be the best of a number of reducing agents tried. The reduction of riboflavin to the non-fluorescent state by stannous chloride took place rapidly only under the influence of ultra-violet radiations. This observation supports the contention of Haring and Walton (6) that the autoxidation of stannous chloride is a photochemical chain reaction. It was found necessary to twice recrystallize the stannous chloride from hot 95% ethanol to remove impurities that cause turbidity. In the analysis of many materials, pure benzyl alcohol gave exactly the same instrument reading as a blank prepared by reduction with stannous chloride. However, some extracts contained substances other than riboflavin that were extracted by benzyl alcohol and exhibited a yellowish fluorescence in ultra-violet light that was not abolished by stannous chloride. In such cases a significant error was introduced when pure benzyl alcohol was used as the blank, and therefore a blank prepared by treating an aliquot of the test solution with stannous chloride must be employed.

The fluorescence measurements were made with the instrument described by Froman and McFarlane (4), employing a Corning red-purple Corex No. 986 filter between the ultra-violet lamp and the solution. A Corning No. 511 filter gave a smaller reading with the blank and a greater galvanometer deflection for the same concentration of riboflavin, but the reduction of riboflavin by stannous chloride in blue light is much slower than in ultra-violet light.

## PROCEDURE

Transfer a 5 to 20 gm. sample, the weight depending on the vitamin content, to a 250 ml. centrifuge bottle and add 50 to 75 ml. of a 0.2% pepsin solution in 0.33% hydrochloric acid. Let stand for one hour in the dark and adjust to pH 2.0 with *N* hydrochloric acid or *N* sodium hydroxide, using thymol blue as an external indicator. Incubate overnight at 37° C. (excluding light), adjust to pH 4.5, using bromcresol green as an external indicator, add 0.1 gm. of takadiastase and incubate in the dark at 37° C. for a further three to four hours. Centrifuge at maximum speed, transfer the supernatant to a 100 ml. volumetric flask; wash the residue twice with distilled water, combine the extract and washings, and dilute to volume with distilled water. Store the extract in the dark until ready to complete the analyses as follows.

Pipette 3 ml. of the extract into each of two 15 ml. graduated centrifuge tubes, and to each add 2 ml. of a saturated aqueous solution of barium chloride and 7 ml. of benzyl alcohol. Shake thoroughly, but not too vigorously, for about one minute and centrifuge at maximum speed for about 10 minutes until the upper benzyl alcohol layer is quite clear. Note the volume of the benzyl alcohol layer and pipette 5 ml. of each into two fluorimeter tubes. To one tube add 0.5 ml. of 95% ethanol and 0.5 ml. of pure benzyl alcohol, and to the other (blank control) add 0.5 ml. of 95% ethanol and 0.5 ml. of a 3% solution of stannous chloride in pure benzyl alcohol.

Invert each tube several times to ensure complete mixing. Place the blank in the instrument (4) and expose to ultra-violet light for approximately three minutes until the galvanometer remains steady. Adjust the galvanometer to zero reading with the blank in position, substitute the test solution, and rotate the polaroids until the galvanometer again reads zero. Replace the

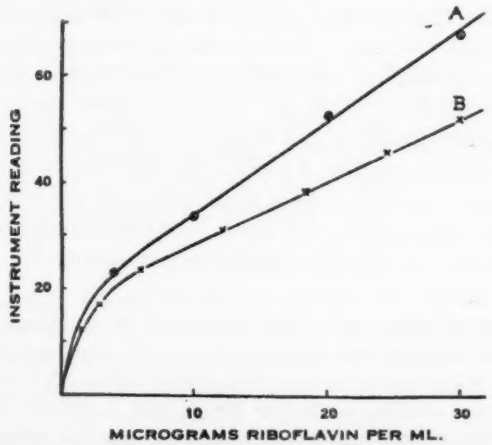


*Fig. 1.—Calibration curves of riboflavin in (a) aqueous solution and (b) benzyl alcohol extract. (This graph also indicates the percentage extraction of riboflavin from aqueous solution by benzyl alcohol.)*

test solution with the blank to ensure that the voltage has not changed appreciably. Convert the polaroid reading to micrograms of riboflavin by reference to a standard calibration curve (Fig. 1) prepared from data obtained with aqueous solutions of pure riboflavin treated in a manner identical with that of the actual test. Calculate the riboflavin content as follows:—

$$A \times 6 \times B/5 \times 100/3 \times 1/C = \text{micrograms per gm.}$$

where $A$ = reference graph reading in micrograms per millilitre,
$B$ = volume of the benzyl alcohol layer,
$C$ = weight of original sample in grams,
6 = ml. of solution taken for test.

The data in Fig. 1 also indicate the percentage extraction of riboflavin from aqueous solutions by benzyl alcohol. The percentage extraction varies with the concentration, and hence the value of $K$ in the equation

$$C = K \sin^2 \theta$$

is a variable quantity (4).

The writers have found that waste benzyl alcohol can be very satisfactorily reclaimed by the following procedure. Add a 20% solution of trichloracetic acid to give a 10% solution in benzyl alcohol. Shake, centrifuge, and siphon off the benzyl alcohol from the aqueous layer. Filter the benzyl alcohol and distill. The use of a fractionating column is unnecessary in the distillation.

## Results

Recovery experiments were conducted on a number of products with the results shown in Table I. The readings obtained on different aliquots of

TABLE I

REPRODUCIBILITY OF THE READINGS OBTAINED WITH DIFFERENT ALIQUOTS OF THE SAME EXTRACT, AND RECOVERY OF RIBOFLAVIN ADDED TO DIFFERENT PRODUCTS

| Material | Instrument reading | | Micrograms per ml. | Riboflavin added, micrograms | Recovery of riboflavin, % |
|---|---|---|---|---|---|
| Liver meal | *(a)** | 20.7 | 0.54 | | |
| | *(b)* | 20.1 | 0.51 | 30.0 | 100.5 |
| | *(c)* | 20.1 | 0.51 | | |
| Skim-milk powder | *(a)* | 12.5 | 0.14 | | |
| | *(b)* | 12.4 | 0.14 | 25.0 | 97.3 |
| | *(c)* | 12.5 | 0.14 | | |
| Bread | *(a)* | 11.3 | 0.12 | | |
| | *(b)* | 11.9 | 0.13 | 21.8 | 97.6 |
| | *(c)* | 12.0 | 0.13 | | |
| Yeast | *(a)* | 11.1 | 0.12 | | |
| | *(b)* | 11.2 | 0.12 | 21.8 | 97.6 |
| | *(c)* | 10.8 | 0.12 | | |
| Whey powder | | 13.1 | 0.16 | 21.8 | 93.5 |

* *Aliquots of the same extract before riboflavin added.*

the same extract were quite constant and the recoveries of added riboflavin good. The sample of whey powder was badly caramelized, and the lower recovery may have been due to interference by pigments.

TABLE II

THE RIBOFLAVIN CONTENT OF VARIOUS MATERIALS AS DETERMINED BY THE MODIFIED METHOD

| Material | Riboflavin, micrograms per gm. | | Material | Riboflavin, micrograms per gm. | |
|---|---|---|---|---|---|
| | Author's method | Range of values given in the literature | | Author's method | Range of values given in the literature |
| Calf liver | 32.0 | 32.0 - 40.0 | Chicken liver | 18.6 | — |
| Bran | 2.7 | 3.17 | Egg yolk | 5.2 | 5.0 - 6.0 |
| Whole wheat flour | 1.7 | 0.89 - 2.03 | Egg white | 3.1 | 4.0 - 5.0 |
| Buttermilk powder | 31.3 | — | Grass clippings | 1.8 | 0.5 - 1.4 |
| Dried yeast | 18.7 | 18.0 - 21.0 | Whole milk | 1.0 | 1.0 - 3.0 |
| Skim-milk powder | 26.4 | 19.0 - 29.0 | Whey powder | 28.1 | 18.1 - 25.0 |

The possibility of destruction of riboflavin during enzymatic digestion was checked by carrying out the entire procedure with a pure riboflavin solution, and 98.5% of the riboflavin was recovered. The riboflavin content of a variety of materials as determined by the modified procedure is given in Table II. The simultaneous estimation of riboflavin and thiamine (7) has been carried out on aliquots of the same extract of various materials with satisfactory results.

## Acknowledgment

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# THE ALKALOIDS OF *LYCOPODIUM* SPECIES

## I. *LYCOPODIUM COMPLANATUM* L.[1]

BY RICHARD H. F. MANSKE[2] AND LÉO MARION[2]


### Abstract

*Lycopodium complanatum* L. has yielded a total of eight alkaloids, six of which appear to be new. They are complanatine (L1) ($C_{15}H_{31}ON$); alkaloid L2 ($C_{18}H_{29}O_2N$); alkaloid L3 ($C_{18}H_{31}O_2N$); alkaloid L4 ($C_{16}H_{27}N$); alkaloid L5 ($C_{18}H_{28}O_2N_2$); obscurine (L6) ($C_{15}H_{28}ON_2$); the known lycopodine ($C_{16}H_{25}ON$); and nicotine. It is pointed out that this is the first recorded occurrence of nicotine in a pteridophyte. The isolation of nicotine from *Equisetum arvense* L. is also recorded.


Vascular plants are divided into two great divisions, Pteridophyta and Spermatophyta. Chemists have devoted most of their energies to the chemical examination of plants belonging to the latter division, i.e., the flowering plants. The pteridophyta, sometimes called vascular cryptogams, are of secondary economic importance and frequently inconspicuous in appearance. They have received comparatively little attention from chemists. Certainly only a very few alkaloids from this source have been obtained in a pure state, and the constitution of none of these had until now been determined.

The family Lycopodiaceae includes the monotypic Australian genus *Phyloglossum* and the ubiquitous genus *Lycopodium* comprising some 180 species. The authors have examined five species native to the western extremes of the Lautentian Plateau and now report on the alkaloids isolated from *L. complanatum* L. The same plant was first examined in 1881 by Bödeker (2) who reported the occurrence of an alkaloid, lycopodine, to which he assigned the formula $C_{32}H_{52}O_2N_2$. Recently Achmatowicz and Uzieblo (1) gave the same name to one of three alkaloids that they isolated from *L. clavatum* L. They assigned the formula $C_{16}H_{25}ON$ to the base, which melted at 114 to 115° C. as recorded by Bödeker. It has now been shown that the chief alkaloids from these two plants of American origin are identical and presumably also identical with the lycopodine of previous authors. The same alkaloid has now been found in several other species. It yields analytical figures in best agreement with $C_{16}H_{25}ON$.

It has been possible to isolate a total of eight alkaloids from *L. complanatum*. In order to avoid cumbersome and perhaps inappropriate names, it has been deemed expedient to designate the individual alkaloids by a number following the capital L. Where the homogeneity and purity of the bases do not seem to be in doubt, a trivial name may also be given. Thus alkaloid L1, best represented by $C_{15}H_{31}ON$, has been termed complanatine. The empirical formula of L1 and those of L2 ($C_{18}H_{29}O_2N$), of L3 ($C_{18}H_{31}O_2N$), and of L4

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*Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1052.*

[2] *Chemist.*

($C_{16}H_{27}N$) make it probable that these alkaloids are closely related to lycopodine. On the other hand, two new alkaloids, containing two nitrogen atoms each, may ultimately prove to possess a radically different structure. One of these, L6 ($C_{18}H_{28}ON_2$), has been termed obscurine since it was first obtained from *L. obscurum*. The other, L5 ($C_{18}H_{28}O_2N_2$), is empirically closely related to obscurine but has been found only in *L. complanatum*. It may be pointed out that the above formulae are mostly based on analyses of the perchlorates. Exclusive of lycopodine and complanatine there was available less than 1 gm. of each of the bases. When more material becomes available, efforts to confirm the formulae will be made.

Lastly, the occurrence of nicotine in this plant is reported. The total amount present is of the order of parts per million of the dried plant. Some, but not all, of the other species have also yielded nicotine. Furthermore, the authors have found it in *Equisetum arvense* L., although the total yield of alkaloids from this plant is extremely small and no other bases could be obtained in a pure state. The occurrence of nicotine in a number of flowering plants is now a matter of common knowledge. Aside from its presence in *Nicotiana* and *Duboisia* species it has recently been found in *Asclepias syriaca* L. (3). The occurrence of the same alkaloid in distantly related plants is no longer considered astonishing. Nevertheless, nicotine is the only alkaloid that has bridged the gap between Pteridophyta and Spermatophyta, it being present in no fewer than four orders, namely, Equisetales, Lycopodiales, Gentianales, and Polemoniales.

The authors have also investigated, but only in a preliminary way, the nature of the water insoluble polysaccharides of the plant. Hydrolysis with boiling dilute sulphuric acid yielded an appreciable amount of galactose. A search for fucose, and mannose, sugars present in the polysaccharide of marine algae, proved negative.

## Experimental

The material, which was collected in October, was air-dried, ground to suitable size, and extracted in Soxhlet apparatus with methanol. There was available 65 kg. The following procedure has been adopted as standard in the investigation of all *Lycopodium* species thus far examined. It is given in considerable detail because it is not intended to repeat it in later communications.

### *Procedure*

The methanolic extract was largely freed of methanol, water was added, and the remainder of the solvent boiled off. Hydrochloric acid was added until the mixture was distinctly acid to Congo red. Hot water was added until the volume was approximately one litre for every three kilos of plant material. The thoroughly stirred mixture was allowed to cool slowly and to stand undisturbed for several days. At the end of this time it was possible to decant a reasonably clear aqueous solution from the semisolid mixture of fats and other water insoluble substances. (In the case of *L. lucidulum* the

insoluble matter remained in suspension but it proved to be unusually easy to filter and wash.) The insoluble residues were heated again with very dilute hydrochloric acid, the mixture was allowed to cool, and the decantate added to the next lot. The aqueous extract was filtered through a layer of charcoal, basified with excess ammonia, and repeatedly extracted with chloroform. The solvent was removed from the extract and the residue heated with an excess of dilute hydrochloric acid. The cooled solution was filtered with the aid of charcoal and extracted with ether until nothing further was removed. The aqueous solution was then basified with ammonia, and the liberated bases were extracted with several portions of ether. (The bases from *L. lucidulum* are not completely soluble in ether, and the ether insoluble portion was subsequently extracted with chloroform.) The combined extract was washed with water, the solvent removed, and the residue dried *in vacuo*. This will be referred to as the 'crude alkaloid'.

*Lycopodine*

The crude alkaloid was slowly distilled *in vacuo*, the distillation flask being heated in an air bath. The following fractions were collected—

(I) 85 to 95° (2 mm.)
(II) 150 to 160° (3 mm.)
(III) 175 to 185° (2 mm.)
(IV) Residue.

Fraction (II) was dissolved in ether and inoculated with a crystal of lycopodine. The crystals were filtered off, washed with ether, and recrystallized first from dry ether and then from hexane. As thus obtained, lycopodine melts not quite sharply at 116°.* By working up the mother liquors by further crystallization and distillation it was possible to obtain a satisfactory amount of crystalline base, but until it was observed that most of the lycopodium alkaloids form crystallizable perchlorates complete separation was not accomplished. The perchlorate of lycopodine is sparingly soluble in methanol or water and virtually insoluble in acetone and other organic solvents. It crystallizes from hot water in brilliant prisms that melt with some decomposition at 283° C. but without appreciable previous charring or shrinking. Found: C, 77.73; H, 10.38; N, 6.00, 6.01%. Calc. for $C_{16}H_{25}ON$: C, 77.73; H, 10.12; N, 5.66%. The perchlorate crystallizes without solvent of crystallization. Found: C, 55.51, 55.66; H, 7.72, 7.65; N, 3.92, 4.13%. Calc. for $C_{16}H_{25}ON \cdot HClO_4$: C, 55.25; H, 7.48; N, 4.03%.

*Complanatine* (L1)

The combined mother liquor from the crystallization of the lycopodine was freed of solvent and the viscous residue dissolved in methanol-acetone. A 60% aqueous solution of perchloric acid was added, drop by drop, until the mixture was just acid to Congo red. The copious crop of lycopodine perchlorate, which readily crystallized, was filtered off and washed with

* *All melting points are corrected.*

acetone. One recrystallization from methanol or from water served to yield a pure compound.

The filtrate was concentrated somewhat and treated with ethyl acetate until the incipient turbidity just disappeared on mixing. The perchlorate, which then crystallized, was filtered off, washed with ethyl-acetate–acetone, and redissolved in acetone. A small amount of undissolved lycopodine perchlorate was filtered off and the concentrated filtrate treated with ethyl acetate. The complanatine perchlorate thus obtained melted sharply at 194° C. It is moderately soluble in hot water and crystallizes in brilliant polyhedra from this solvent. Yield, 8 gm. It contains one molecule of water of crystallization, which is only slowly lost at 110° (2mm.) and rapidly reabsorbed on exposure to air. Found: C, 54.55, 54.41; H, 8.48, 8.16%. Calc. for $C_{18}H_{31}ON \cdot HClO_4 \cdot H_2O$: C, 54.61; H, 8.60%.

The free base was regenerated by treating an aqueous suspension of the perchlorate with ammonia and shaking with ether. The washed solution on evaporation to a small volume deposited colourless needles, which, when washed with ether and recrystallized from acetone-ether, melted sharply at 169° C. Found: C, 77.61; 77.21; H, 11.31, 10.97; N, 5.05%. Calc. for $C_{18}H_{31}ON$ : C, 77.98; H, 11.19; N, 5.05%.

*Alkaloid L2*

The acetone–ethyl-acetate mother liquor from which the lycopodine and the complanatine had been obtained was diluted with water, boiled to expel organic solvents, and filtered while hot. The cooled solution deposited a sparingly soluble perchlorate which, when recrystallized twice more from hot water, was obtained in brilliant stout prisms that melted sharply and without decomposition at 231° C. The perchlorate of alkaloid L2 thus obtained did not lose any weight when heated at 110° (1 mm.) for five hours. Found: C, 55.39; 55.24; H, 7.82, 7.72; N, 3.64%. Calc. for $C_{18}H_{29}O_2N \cdot HClO_4$: C, 55.17; H, 7.66; N, 3.58%.

A small portion of the salt was decomposed with aqueous sodium hydroxide in the presence of purified ether. The washed solution was evaporated to dryness and the residue recrystallized from purified pentane in which it is moderately soluble. Colourless flat prisms of alkaloid L2 melting sharply at 97° C. were thus obtained. Found: C, 74.55; H, 10.09; N, 4.91%. Calc. for $C_{18}H_{29}O_2N$: C, 74.23; H, 9.97; N, 4.81%.

*Alkaloid L3*

The free bases were regenerated from the aqueous mother liquors from alkaloid L2 and reconverted to perchlorates in concentrated aqueous solution, which on cooling deposited an oily perchlorate. This was washed with cold water by decantation, and it then slowly became crystalline. When it was recrystallized twice from hot water it consisted of brilliant colourless elongated plates that melted sharply at 246° C. Found: C, 55.50, 55.26; H, 8.10, 7.85; N, 3.55%. Calc. for $C_{18}H_{31}O_2N \cdot HClO_4$ : C, 54.90; H, 8.13; N, 3.55%.

*Alkaloid L4*

The aqueous mother liquor from the above perchlorate was concentrated somewhat, filtered (charcoal), and cooled. The perchlorate, which slowly separated, was recrystallized twice from hot water. It was then obtained in pearly plates that melted sharply at 225° C. Found: C, 55.97, 56.17; H, 8.39; 8.12; N, 4.12%. Calc. for $C_{16}H_{27}N \cdot HClO_4 \cdot \frac{1}{2}H_2O$: C, 56.06; H, 8.47; N, 4.09%. At 130° C. the substance lost 3.25% of its weight; $\frac{1}{2}H_2O$ requires 2.63%.

*Alkaloid L5*

The fraction, b.p. 175 to 185° C. (2 mm.) was redistilled and a fraction boiling at 196° (2 mm.) collected separately. It was dissolved in hot dilute perchloric acid and the filtered (charcoal) solution cooled. The crystals, which separated in the course of several days, were recrystallized from hot water; they were obtained in brilliant colourless polyhedra that melted with slight previous darkening at 282° C. Found: C, 55.53, 55.45; H, 8.32, 7.77; N, 6.76, 7.19%. Calc. for $C_{18}H_{25}O_2N_2 \cdot HClO_4$: C, 55.61; H, 7.64; N, 7.21%. There was no loss in weight at 110° (1 mm.). A further small amount of this perchlorate was obtained from the undistilled residue from which the obscurine had been crystallized. In this case the salt was recrystallized from hot methanol, in which it is only sparingly soluble. The melting point of this perchlorate (L5) is close to that of lycopodine perchlorate. It is therefore of interest to note that a mixture of the two salts was completely liquid at 260° C. Other perchlorates that melt at temperatures reasonably close to each other have been mixed, and in all cases a substantial lowering of melting points has been observed.

*Obscurine (L6)*

The undistilled residue was dissolved in hot aqueous oxalic acid and the filtered solution extracted with ether. It was then basified with ammonia and the liberated bases were taken up in a large volume of ether. The washed ether solution was evaporated to dryness and the residue dissolved in methanol. The small crop of crystals (0.05 gm.) that separated in the course of several days was filtered off (m.p. 280° C.) and recrystallized from chloroform-methanol, in the latter of which it is sparingly soluble. Colourless needles of obscurine were thus obtained which melted at 282° C. either alone or in admixture with a specimen of alkaloid similarly obtained from *L. obscurum*. Found: C, 74.50, 74.92; H, 9.64, 9.55; N, 9.66, 9.76%. Calc. for $C_{18}H_{28}ON_2$: C, 75.00; H, 9.72; N, 9.72%.

The perchlorate was recrystallized from acetone–ethyl-acetate; it melted with some previous decomposition at 299° C. It is readily soluble in methanol, acetone, and water. The analyses indicate that both nitrogens are basic and one molecule of water was lost at 130° (1 mm.). Found: C, 42.45; H, 6.65; N, 5.08; $H_2O$, 3.12%. Calc. for $C_{18}H_{28}ON_2 \cdot 2HClO_4 \cdot H_2O$: C, 42.61; H, 6.31; N, 5.52; $H_2O$, 3.55%.

*Nicotine*

The low boiling fraction consisted of a colourless oil with a very strong odour of nicotine. It was dissolved in methanol and treated with an excess of picric acid. The sparingly soluble picrate, which crystallized at once, melted at 225° C. It was recrystallized from hot methanol, and it then melted at 226° C. either alone or in admixture with an authentic specimen of nicotine dipicrate. Calc. for $C_{22}H_{20}O_{14}N_8$; N, 18.06%. Found: N, 18.10%.

The fraction of the same boiling point from *Equisetum arvense* was treated in the same manner, and it yielded nicotine dipicrate of equal purity.

The nicotine was regenerated from the picrate and converted to the dipicrolonate, which, when recrystallized from aqueous acetone, melted at 228° C. either alone or in admixture with a specimen of known authenticity. It is estimated that nicotine was present to the extent of 2 p.p.m.

It may be noted that repeated attempts to prepare crystalline picrates from the other *Lycopodium* bases and particularly from lycopodine yielded only sparingly soluble resins.

*Hydrolysis of Water Insoluble Polysaccharide*

One kilo of the plant material that had been extracted with methanol was soaked in 5 litres of 1% hydrochloric acid overnight. The mixture was filtered and the residue washed with water until the filtrate gave only a slight opalescence with silver nitrate. It was then heated under reflux for two hours with 2% sulphuric acid. The aqueous solution was quantitatively freed of sulphuric acid by means of barium hydroxide and then evaporated to a thick syrup *in vacuo*. The residue was extracted with a litre of hot methanol and the filtered solution evaporated once more *in vacuo* to a thin syrup. Methanol was added until further additions produced no more turbidity. The clear solution was evaporated to about 100 cc. and allowed to remain in a cool place for several weeks. The solid crystalline sugar was filtered off, washed with methanol, and recrystallized from a large volume of boiling methanol. There was obtained 8 gm. of colourless, anhydrous *d*-galactose, which melted at 165° C. either alone or in admixture with an authentic specimen. The phenylosazone was recrystallized from methanol, and it melted at 193° C. either alone or in admixture with *d*-galactose phenylosazone.

An attempt to isolate a sparingly soluble phenylhydrazone (fucose, mannose) from the galactose mother liquor was unsuccessful.

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